This chapter presents the pulsed laser deposition technique used for the growth of hydroxyapatite thin films on TiAl₆V₄ implant material. The chapter gives an overview of the anodization process used. The various characterization tools employed for analyzing the films are also described here.

2.1 Classification of Deposition Technologies

Basically, thin-film deposition technologies are either purely physical, such as evaporative methods, or purely chemical, such as gas- and liquid-phase chemical processes. A considerable number of processes that are based on glow discharges and reactive sputtering combine both physical and chemical reactions; these overlapping processes can be categorized as physical-chemical methods [1, 2].

A classification scheme is presented in Table 2.1 [1], where thin-film deposition technologies are grouped according to evaporative methods, glow discharge, gas-phase chemical, and liquid-phase chemical processes.
Table 2.1: Classification of the deposition processes.

<table>
<thead>
<tr>
<th>Classification</th>
<th>Type</th>
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<tbody>
<tr>
<td>Evaporative methods</td>
<td>Conventional vacuum evaporation</td>
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<tr>
<td>(Vacuum Evaporation)</td>
<td>Molecular–beam epitaxy (MBE)</td>
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<tr>
<td></td>
<td>Electron Beam evaporation</td>
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<td></td>
<td>Pulsed laser deposition</td>
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<tr>
<td>Glow – Discharge Processes (Sputtering-Plasma process)</td>
<td>Diode sputtering</td>
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<td></td>
<td>Reactive sputtering</td>
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<td>Plasma oxidation</td>
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<td></td>
<td>Bias sputtering</td>
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<td></td>
<td>Plasma anodization</td>
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<td></td>
<td>Magnetron sputtering</td>
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<td></td>
<td>Ion beam sputter deposition</td>
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<td></td>
<td>Microwave ECR plasma</td>
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<td></td>
<td>CVD Cluster beam deposition</td>
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<tr>
<td>Gas-phase chemical process</td>
<td>CVD Epitaxy thermal oxidation</td>
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<tr>
<td>(Chemical vapour deposition)</td>
<td>Atmospheric-pressure CVD</td>
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<td>Thermal nitridation</td>
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<td>Low-pressure CVD</td>
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<td>Thermal polymerization</td>
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<td>Metalorganic CVD</td>
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<td></td>
<td>Laser-induced CVD (PCVD)</td>
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<td></td>
<td>Electron-enhanced CVD</td>
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<td></td>
<td>Ion implantation</td>
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<tr>
<td>Liquid phase chemical techniques</td>
<td>Electroplating</td>
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<tr>
<td>(Electro Processes - Mechanical Techniques)</td>
<td>Spray pyrolysis</td>
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<td></td>
<td>Electroless plating</td>
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<td></td>
<td>Spray-on techniques</td>
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<td></td>
<td>Electrolytic anodization</td>
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<td></td>
<td>Chemical reduction plating</td>
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<td></td>
<td>Electrophoretic deposition</td>
</tr>
<tr>
<td></td>
<td>Liquid phase epitaxy</td>
</tr>
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</table>
2.1.1 Overview of various thin film deposition process.

A brief description of the principles, salient features and applications for some of the important thin-film deposition processes are given below.

i) Evaporative Technologies

One of the oldest techniques used for depositing thin films, thermal evaporation or vacuum evaporation is still widely used in the laboratory and in industry for depositing metal and metal alloys [1,3]. The following sequential basic steps take place: (i) a vapor is generated by boiling or subliming a source material (ii) the vapor is transported from the source to the substrate and (iii) the vapor is condensed to a solid film on the substrate surface. Evaporants cover an extraordinary range of varying chemical reactivity and vapor pressures. This variety leads to a large diversity of source components including resistance-heated filaments, electron beams; crucibles heated by conduction, radiation, or rf-induction; arcs, exploding wires, and lasers. Additional complications include source-container interactions, requirements for high vacuum, precise substrate motion (to ensure uniformity) and the need for process monitoring and control.

a) Molecular Beam Epitaxy. MBE is a sophisticated, finely controlled method for growing single-crystal epitaxial films in a high vacuum. The films are formed on single-crystal substrates by slowly evaporating the elemental or molecular constituents of the film from separate Knudsen effusion source cells (deep crucibles in furnaces with cooled shrouds) onto substrates held at a temperature appropriate for chemical reaction, epitaxy, and re-evaporation of excess reactants [3]. The furnaces produce atomic or molecular beams of relatively small diameter, which are directed at the heated substrate, usually silicon or gallium arsenide. Fast shutters are interposed between the sources and the substrates. By controlling these
shutters, one can grow super lattices with precisely controlled uniformity, lattice match, composition, dopant concentrations, thickness, and interfaces down to the level of atomic layers.

b) **Electron beam evaporation:** In electron beam evaporation (EBE) a stream of electrons is accelerated through fields of typically 5–10kV and focussed onto the surface of the material for evaporation. The electrons lose their energy very rapidly upon striking the surface and the material melts at the surface and evaporates. That is, the surface is directly heated by impinging electrons, in contrast to conventional heating modes. Direct heating allows the evaporation of materials from water-cooled crucibles. Such water-cooled crucibles are necessary for evaporating reactive and in particular reactive refractory materials to avoid almost completely the reactions with crucible walls. This allows the preparation of high purity films because crucible materials or their reaction products are practically excluded from evaporation. Electron beam guns can be classified into thermionic and plasma electron categories. In the former type the electrons are generated thermionically from heated refractory metal filaments, rods or disks. In the latter type, the electron beams are extracted from plasma confined in a small space.

c) **Laser Induced Evaporation/Laser Ablation/Pulsed Laser Deposition (PLD).** This technique with many names was first used by Smith and Turner in 1965 to deposit thin films in a vacuum chamber using a pulsed ruby laser [1, 3]. In this technique, material is vaporized and ejected from the surface of a target as it irradiated by a laser beam. Films are formed by condensing the material ablated from the target onto a solid substrate. Absorption characteristics of the material to be evaporated determine the laser wavelength to be used. To obtain the high power density required in many
cases, pulsed laser beams are generally employed. Pulse width, repetition rate, and pulse intensity are selected for specific applications.

**ii) Glow-Discharge Technologies**

The electrode and gas-phase phenomena in various kinds of glow discharges (especially rf discharges) represent a rich source of processes used to deposit and etch thin films\[1,4,5\]. Creative exploitation of these phenomena has resulted in the development of many useful processes for film deposition (as well as etching), as listed in Table 2.1.

**a) Sputtering.** The most basic and well-known of these processes is sputtering, the ejection of surface atoms from an electrode surface by momentum transfer from bombarding ions to surface atoms. From this definition, sputtering is clearly an etching process, and is, in fact, used as such for surface cleaning and for pattern delineation. Since sputtering produces a vapor of electrode material, it is also (and more frequently) used as a method of film deposition similar to evaporative deposition. *Sputter deposition* has become a generic name for a variety of processes.

*Diode Sputtering.* Diode sputtering uses a plate of the material to be deposited as the cathode (or rf-powered) electrode (target) in a glow discharge. Material can thus be transported from the target to a substrate to form a film. Films of pure metals or alloys can be deposited when using noble gas discharges (typically Argon) with metal targets.

*Reactive Sputtering.* Compounds can be synthesized by reactive sputtering, that is, sputtering elemental or alloy targets in reactive gases; alternatively, they can be deposited directly from compound targets.

*Bias Sputtering.* Bias sputtering or ion-plating is a variant of diode sputtering in which the substrates are ion bombarded during deposition and prior to film
deposition to clean them. Ion bombardment during film deposition can produce one or more desirable effects, such as resputtering of loosely-bonded film material, low-energy ion implantation, desorption of gases, conformal coverage of contoured surface, or modification of a large number of film properties. The source material need not originate from a sputtering target, but can be an evaporation source, a reactive gas with condensable constituents, or a mixture of reactive gases with condensable constituents and other gases that react with the condensed constituents to form compounds.

All glow discharge processes involve sputtering in one form or another, since it is impossible to sustain a glow discharge without an electrode at which these processes occur. In “electrodeless” discharges, rf power is capacitively coupled through the insulating wall of a tubular reactor. In this case, the inside wall of the tube is the main electrode of the discharge.

**Magnetron Sputtering.** Another variant in sputtering sources uses magnetic fields transverse to the electric fields at sputtering-target surfaces. This class of processes is known as magnetron sputtering. Sputtering with a transverse magnetic field produces several important modifications of the basic processes. Target-generated secondary electrons do not bombard substrates because they are trapped in cycloidal trajectories near the target, and thus do not contribute to increased substrate temperature and radiation damage. This allows the use of substrates that are temperature-sensitive (for example, plastic materials) and surface sensitive (for example, metal-oxides-semiconductor devices) with minimal adverse effects. In addition, this class of sputtering sources produces higher deposition rates than conventional sources and lends itself to economic, large-area industrial application. There are cylindrical, conical, and planar magnetron sources, all with particular advantages and disadvantages for specific applications. As with other forms of sputtering, magnetron sources can
be used in a reactive sputtering mode. Alternatively, one can forego the low-temperature and low radiation-damage features and utilize magnetron sources as high-rate sources by operating them in a bias-sputtering mode.

**Ion-Beam Sputtering.** Ion beams, produced in and extracted from glow discharges in a differentially pumped system, are important to scientific investigations of sputtering, and are proving to be useful as practical film-deposition systems for special materials on relatively small substrate areas. There are several advantages of ion-beam sputtering deposition. The target and substrate are situated in a high-vacuum environment rather than in a high-pressure glow discharge. Glow discharge artifacts are thereby avoided, and higher-purity films usually result. Reactive sputtering and bias sputtering with a separate ion gun can be used.

### iii) Plasma Processes

The fact that some chemical reactions are accelerated at a given temperature in the presence of energetic reactive-ion bombardment is the basis of processes for surface treatments such as plasma oxidation, plasma nitriding, and plasma carburizing [1, 6, 7]. A metal to be oxidized, nitrided or carburized is made the cathode of a glow discharge and is simultaneously heated by radiant or rf-induction means. Protective coatings on a variety of metals can be produced in this way to render surfaces hard and/or corrosion resistant.

**a) Anodization.** Plasma anodization is a technique for producing thin oxide films (less than 100 nm) on metals such as aluminium, tantalum, titanium, and zirconium, collectively referred as *valve metals*. In this case, a dc discharge is set up in an oxygen atmosphere and the substrates (shielded from the cathode to avoid sputter deposition) are biased positively with respect to the anode. This bias extracts negative oxygen ions from the discharge to the surface, which is also bombarded with
electrons that assist the reaction. The process produces very dense, defect-free, amorphous oxide films that are of interest as gate material in compound semiconductor devices such as in microwave field-effect transistors.

b) **Microwave Electron Cyclotron Resonance Deposition.** ECR plasma deposition employs an electron cyclotron resonance (ECR) ion source to create high-density plasma. The plasma is generated by resonance of microwaves and electrons through a microwave discharge across a magnetic field. The main feature of this recently introduced process is the high rate of deposition obtained at a low temperature of deposition.

c) **Cluster Beam Deposition.** Ionized cluster beam deposition (ICB) or cluster beam deposition is one of the most recent emerging technologies for the deposition of thin films with growth-control capabilities not attainable by other processes. ICB deposition is one of several techniques classified as ion-assisted thin-film formation. The material to be deposited emerges and expands into a vacuum environment from a small nozzle of a heated confinement crucible, usually constructed of high-purity graphite. The vapor pressure within the crucible is several orders of magnitude higher than the pressure of the vacuum chamber so that the expanding vapour super cools. Homogeneous nucleation results in the generation of atomic aggregates or clusters of up to a few thousand atoms held together by weak inter atomic forces. The clusters passing through the vacuum towards the substrate can, in part, be positively charged by impact ionization with electron beam irradiation. Closely controlled accelerating voltages add energy to the ionized clusters which then impinge on the substrate, diffuse or migrate along
the plane of the surface, and finally form a thin film of exceptional purity.

iv) Gas-Phase Chemical Processes

Methods of film formation by purely chemical processes in the gas or vapor phases include chemical vapor deposition and thermal oxidation. Chemical vapor deposition (CVD) is a materials synthesis process whereby constituents of the vapor phase react chemically near or on a substrate surface to form a solid product [1,8,9,10]. The deposition technology has become one of the most important means for creating thin films and coatings of a very large variety of materials essential to advanced technology, particularly solid-state electronics where some of the most sophisticated purity and composition requirements must be met. The main feature of CVD is its versatility for synthesizing both simple and complex compounds with relative ease at generally low temperatures. Both chemical composition and physical structure can be tailored by control of the reaction chemistry and deposition conditions. Fundamental principles of CVD encompass an interdisciplinary range of gas-phase reaction chemistry, thermodynamics, kinetics, transport mechanisms, film growth phenomena, and reactor engineering. Chemical reaction types basic to CVD include pyrolysis (thermal decomposition), oxidation, reduction, hydrolysis, nitride and carbide formation, synthesis reactions, disproportionation, and chemical transport. A sequence of several reaction types may be involved in more complex situations to create a particular end product. Deposition variables such as temperature, pressure, input concentrations, gas flow rates and reactor geometry and operating principle determine the deposition rate and the properties of the film deposit. CVD has become an important process technology in several industrial fields and CVD
has long been used for coating of substrates at reduced pressure, often at high temperatures.

**a) Vapor-Phase Epitaxy.** Vapor-phase epitaxy (VPE) and metal-organic chemical vapor deposition (MOCVD) are used for growing epitaxial films of compound semiconductors in the fabrication of optoelectronic devices. Composite layers of accurately controlled thickness and dopant profile are required to produce structures of optimal design for device fabrication.

**b) Photo-Enhanced Chemical Vapor Deposition (PHCVD).** PHCVD is based on activation of the reactants in the gas or vapour phase by electromagnetic radiation, usually short-wave ultraviolet radiation. Selective absorption of photonic energy by the reactant molecules or atoms initiates the process by forming reactive free-radical species that then interact to form a desired film product. Mercury vapor is usually added to the reactant gas mixture as a photosensitizer that can be activated with the radiation from a high-intensity quartz mercury resonance lamp (253.7 nm wavelength). The excited mercury atoms transfer their energy kinetically by collision with the reactants to generate free radicals.

**c) Laser-Induced Chemical Vapor Deposition (LCVD).** LCVD utilizes a laser beam for highly localized heating of the substrate that then induces film deposition by CVD surface reactions. Another mode of utilizing laser (or electron radiation) is to activate gaseous reactant atoms or molecules by their absorption of the specific wavelength of the photonic energy supplied. The resulting chemical gas phase reactions are very specific, leading to highly pure film deposits.
v) **Liquid-Phase Chemical Formation**

The growth of inorganic thin films from liquid phases by chemical reactions is accomplished primarily by electrochemical processes (which include anodization and electroplating), and by chemical deposition processes (which include reduction plating, electroless plating, conversion coating, and displacement deposition) [1,11]. A number of extensive reviews of these film formation processes discuss theory and practice. Another class of film forming methods from the liquid phase is based on chemically reacting films that have been deposited by mechanical techniques. Finally, liquid phase epitaxy is still being used for growing a number of single-crystal semiconductors.

a) **Electrolytic Anodization.** In anodization, as in thermal oxidation, an oxide film is formed from the substrate. The anode reacts with negative ions from the electrolyte in solution and becomes oxidized, forming an oxide or a hydrated oxide coating on semiconductors and on a few specific metals, while hydrogen gas is evolved at the cathode. Nonporous and well adhering oxides can be formed on aluminium, tantalum, niobium, titanium, zirconium, and silicon. The most important applications are corrosion protective films and decorative coatings with dyes on aluminium and its alloys, and layers for electrical insulation for electrolyte capacitors on aluminium and tantalum.

b) **Electroplating.** In electroplating a metallic coating is electrodeposited on the cathode of an electrolytic cell consisting of a positive electrode (anode), a negative electrode (cathode), and an electrolyte solution (containing the metal ions) through which electric current flows. The quantitative aspects of the process are governed by Faraday’s laws. Important electroplating variables include current efficiency, current
density, current distribution, pH, temperature, agitation, and solution composition. Numerous metals and metal alloys have been successfully electroplated from aqueous solutions. Electroplating is widely used in industry and can produce deposits that range from very thin films to very thick coatings (electroforming).

c) **Chemical Reduction Plating.** Chemical reduction plating is based on reduction of a metal ion in solution by a reducing agent added just before use. Reaction is homogeneous, meaning that deposition takes place everywhere in the solution, rather than on the substrate only. Silver, copper, nickel, gold, and some sulfide films are readily plated. The oldest application of the process is the silvering of glass and plastics for producing mirrors using silver nitrate solutions and one of various reducing agents, such as hydrazine.

d) **Electroless Plating.** Autocatalytic or electroless plating is a selective deposition plating process in which metal ions are reduced to a metallic coating by a reducing agent in solution. Plating takes place only on suitable catalytic surfaces, which include substrates of the same metal being plated, hence the definition autocatalysis. Electroless (or electrodeless) plating offers a number of advantages over electroplating, such as selective (patterned) deposition, but is limited to a few metals and some alloys.

e) **Electrophoretic Deposition.** Electrophoretic coating is based on deposition of a film from a dispersion of colloidal particles onto a conductive substrate. The dispersion in a conductive liquid dissociates into negatively charged colloidal particles and positive ions (cations), or the reverse. On application of an electric field between the positive
substrate electrode (anode), the colloidal particles migrate to the substrate, become discharged, and form a film.

**f) Immersion Plating.** Deposition of a metal film from a dissolved salt of the coating metal on a substrate by chemical displacement without external electrodes is known as displacement deposition or immersion plating. Generally, a less noble (more electronegative) metal displaces from solution any metal that is more noble, according to the electromotive force series. Actually, different localized regions on the metal surface become anodic and cathodic, resulting in thicker films in the cathodic areas. The industrial uses of this process are limited to a few applications, mainly thin coatings on copper and its alloys.

**vi) Mechanical Methods**

Mechanical techniques for depositing coatings from liquid media that are subsequently reacted chemically to form the inorganic thin film product are spraying, spinning, dipping and draining, flow coating, roller coating, pressure-curtain coating, brushing, and offset printing of reagent solutions[1,12]. Chemical reaction of the coating residue, often by thermal oxidation, hydrolysis, or pyrolysis (in the case of metal organics) produces the desired solid film. Spin-on deposition of film-forming solutions is widely used in solid-state technology. Liquid spray coating is probably the most versatile mechanical coating technique of the deposition techniques noted, and it is particularly well-suited for high-speed automated mass production. Deposition of very thin films is possible by judicious selection and optimization of spray machine parameters for forming “atomized” droplets and the reagent and solvent systems used to formulate the spray liquid. Spray deposition encompasses several other types of spraying processes that are based on either liquid sources, such as harmonic electrical spraying, or on dry source reactants
that include flame spraying, arc plasma spraying, electric arc spraying, and detonation coating.

a) **Liquid-Phase Epitaxy.** LPE is used for the thermally-controlled overgrowth of thin single-crystalline films of compound semiconductors and magnetic garnets from the melt on a single-crystal substrate. This relatively old and simple technique has been successfully applied in the semiconductor industry for fabricating optoelectronic devices.

**Procedures adopted in the present work:** Pulsed laser deposition was utilised for depositing thin film of hydroxyapatite on TiAl₆V₄ substrates and electrolytic anodizing was adopted for anodization of the TiAl₆V₄ substrates. A detailed description of the above two methods are given below.

**2.1.2 Pulsed laser deposition (PLD)**

Pulsed laser deposition, is a very effective thermal evaporation technique for the preparation of epitaxial films under moderate vacuum, or ultrahigh vacuum conditions [1, 3, 13]. PLD is the deposition method of choice in the case of phase pure growth of multicomponent compositions. PLD technique requires a UV nanosecond pulsed laser source such as the frequency tripled (355 nm) or quadrupled (266 nm) solid state Nd:YAG laser, or the KrF (248 nm) or ArF (193 nm) excimer laser. In a typical PLD process, a focused train of high energy laser pulses, derived from a UV nanosecond pulsed laser source, is rastered over the target. A suitable substrate, often heated, is brought into contact with the laser plume (formed by the high pulse energy beam–target interaction) comprising of atomic and molecular species ablated from the target.
Thin film deposition techniques, anodization of implants and characterization tools used

Figure 2.1. shows a schematic view of a pulsed laser deposition chamber. Provisions are made for controlling the ambient atmosphere within the chamber and substrate heating. Short wavelength irradiation of the target material creates an ablation plume that contacts the substrate.

i) Mechanisms of PLD

The mechanism of pulsed laser deposition, in contrast to the simplicity of the set-up, is a very complex physical phenomenon[13,14,15,16]. It not only involves the physical process of laser-material interaction under the impact of high-power pulsed radiation on solid target, but also the formation of plasma plume with highly energetic species and even the transfer of the ablated material through the plasma plume onto the heated substrate surface. Thus the thin film formation process in PLD generally can be divided into the following four stages.
a) Laser radiation interaction with the target
b) Dynamics of the ablated materials.
c) Deposition of the ablation materials on the substrate.
d) Nucleation and growth of a thin film on the substrate surface

Each stage in PLD is critical to the formation of quality epitaxial, crystalline, stoichiometric and uniform thin film.

In the first stage, the laser beam is focused onto the surface of the target. At sufficiently high flux densities and short pulse duration, all elements in the target are rapidly heated up to their evaporation temperature. Materials are dissociated from the target surface and ablated out with stoichiometry as in the target. The instantaneous ablation rate is highly dependent on the fluences of the laser shining on the target. The ablation mechanisms involve many complex physical phenomena such as collisional, thermal, and electronic excitation, exfoliation and hydrodynamics.

During the second stage, the emitted materials tend to move towards the substrate according to the laws of gas-dynamics. The spot size of the laser and the plasma temperature has significant effects on the deposited film uniformity. The target-to-substrate distance is another parameter that governs the angular spread of the ablated materials. A mask placed close to the substrate could reduce the spreading. The third stage is important to determine the quality of the thin film. The ejected high-energy species impinge onto the substrate surface and may induce various type of damage to the substrate. These energetic species sputter some of the surface atoms and a collision region is formed between the incident flow and the sputtered atoms. Film grows after a thermalized region is formed. The region serves as a source for condensation of particles. When the condensation rate is higher than the rate of particles ejected
by the sputtering, thermal equilibrium condition can be reached quickly and film grows on the substrate surface.

The effect of increasing the energy of the adatoms has a similar effect of increasing substrate temperature on film growth[14]. Typical power densities involved in PLD are approximately 50 MW cm-2 for a reasonable growth rate (> 1 Å/shot). The plasma is formed initially during laser target interaction in vacuum or in air and then again an explicit laser – plasma interaction occurs. Due to which ions in the plasma are accelerated to as much as 100 – 1000 eV. Nucleation-and-growth of crystalline films depends on many factors such as the density, energy, ionization degree, and the type of the condensing material, as well as the temperature and the physio-chemical properties of the substrate. The two main thermodynamic parameters for the growth mechanism are the substrate temperature T and the supersaturation Dm of laser plasma. They can be related by the following equation

$$Dm = kT \ln(R/Re)$$  \hspace{1cm} (2.1)

where k is the Boltzmann constant, R is the actual deposition rate, and Re is the equilibrium value of deposition rate of the thin film at the temperature T. The nucleation process depends on the interfacial energies between the three phases present – the substrate, the condensing material and the vapour. The critical size of the nucleus depends on the driving force, i.e. the deposition rate and the substrate temperature. For the large nuclei, a characteristic of small supersaturation, they create isolated patches (islands) of the film on the substrate, which subsequently grow and coalesce together. As the supersaturation increases, the critical nucleus shrinks until its height reaches on atomic diameter and its shape is that of a two-dimensional layer. For large supersaturation, the layer-by-layer nucleation will happen for incompletely wetted foreign substrates. The crystalline film growth depends on the surface
mobility of the adatom (vapour atoms). Normally, the adatom will diffuse through several atomic distances before sticking to a stable position within the newly formed film. The surface temperature of the substrate determines the adatom's surface diffusion ability. High temperature favours rapid and defect free crystal growth, whereas low temperature or large supersaturation crystal growth may be overwhelmed by energetic particle impingement, resulting in disordered or even amorphous structures. The mean thickness (N99) at which the growing thin and discontinuous film reaches continuity, is given by the formula

$$N99 = A(1/R)^{1/3} \exp (-1/T) \quad (2.2)$$

where $R$ is the deposition rate (supersaturation related) and $T$ is the temperature of the substrate and $A$ is a constant related to the materials.

In the PLD process, due to the short laser pulse duration (~10 ns) and hence the small temporal spread (~10 ms) of the ablated materials, the deposition rate can be enormous (~10 nm/s). Consequently a layer-by-layer nucleation is favoured and ultra-thin and smooth film can be produced. In addition the rapid deposition of the energetic ablation species helps to raise the substrate surface temperature. In this respect PLD tends to demand a lower substrate temperature for crystalline film growth.

Pulsed laser deposition is the main growth technique used in the present study. The deposition was carried out in a vacuum chamber pumped by a turbo-molecular pump (Pfeiffer Vacuum Inc, Germany). The laser used was the third harmonics (355 nm) of Nd:YAG laser (Spectra Physics model GCR 150). In this study TiAl$\textsubscript{6}$V$_4$ substrates have been coated by PLD method at different substrate temperatures ranging from 150-500°C in O$_2$ atmosphere and the films were subjected to a hydrothermal process at 100°C to get polycrystalline films.
2.2 Anodizing

Anodizing is an electrochemical process in which the part is made the anodic (positive) electrode in a suitable electrolyte [11,17,18,19]. Sufficiently high voltage is deliberately applied to establish the desired polarization to deposit oxygen at the surface (O2 overvoltage). The metal surfaces or ions react with the oxygen to produce adherent, oxide coatings.

Industrial anodizing processes are confined mainly to aluminium and to a much lesser extent to magnesium and titanium alloys.

Anodic coating applications include:

a. Protection corrosion, wear and abrasion resistance.

b. Decorative clear coatings on polished or brightened surfaces, dyed (color) coatings.

c. Base for subsequent paint or organic coating.

d. Base for plating aluminium.

e. Special based on some specific property or the coating, e.g. thermal barrier films, refractory films, electrolytic condensers, capacitors (dielectric films).

Titanium anodizing standards such as AMS 2487 define film properties and quality requirements for an electrochemical process that does not exceed 12.4 pH. This pH range covers acid and neutral salt solutions. The acid or neutral salt anodized films are classified as abrasion resistant. AMS 2488 specifics alkaline anodizing solutions with a pH of 13 or greater. Alkaline anodizing creates a thicker oxide film and may be specified as an anti-galling coating for severe wear applications. The composition and structure of alkaline anodized films are unique and some are considered proprietary [19].
The anodic films are classified according to the solvent action of the electrolyte. The films produced in sulphuric or chromic acids are porous type films. Phosphoric acid has even greater solvent action, resulting in oxides with a greater degree of porosity; these coatings are used for adhesive bonding and for plating on aluminium processes to provide deposit adhesion by mechanical locking in the enlarged pores. Less aggressive mild electrolytes such as tartaric acid, ammonium tartarate, boric acid, borate compounds, citric acid, etc., have little or no ability to attack the anodic oxide. These films are essentially non-porous and thin and are considered barrier type coatings.

In an air or moisture containing environment, titanium dioxide (TiOz) spontaneously forms on the surface of CP(Commercially Pure) titanium. The oxide is typically 2 to 5 nanometers thick and this passive layer is responsible for the excellent corrosion resistance of titanium. Anodizing is a well recognized surface modification for titanium and titanium alloys used in the aerospace, chemical processing, and consumer product industries. In the last few years, anodizing has been successfully used as a surface treatment for orthopaedic implants.

Titanium and its alloys are anodized to provide [19]:

1) Protection from galvanic corrosion when assembled or in contact with dissimilar metals by reducing or minimizing potential differences.
2) Anti-galling, anti-fretting properties to the surfaces of parts in moving assemblies.
3) Part identification using a range of integral colors produced by the particular anodizing process.
Thin film deposition techniques, anodization of implants and characterization tools used

Fig 2.2 Set up utilized for the anodization treatments of Ti substrates

TiAl₆V₄ was anodized in 200 g/L sulfuric acid, 5% trisodium phosphate, and 5% sodium bicarbonate (baking soda) at voltages of 55, 60 and 75 volts to yield anodized surfaces of different surface topographies with the set up as shown in figure 2.2.

2.3. Characterization tools

2.3.1. Thin film thickness

Thickness is one of the most important thin film properties to be characterized since it plays an important role in the film properties unlike a bulk
material [20,21]. Reproducible properties are achieved only when the film thickness and the deposition parameters are kept constant. Film thickness may be measured either by in-situ monitoring of the rate of deposition or after the film deposition. The thicknesses of the thin films prepared for the work presented in this thesis were measured by a stylus profiler (Dektak 6M).

i) **Stylus profiler**

The stylus profiler takes measurements electromechanically by moving the sample beneath a diamond tipped stylus. The high precision stage moves the sample according to a user defined scan length, speed and stylus force. The stylus is mechanically coupled to the core of a linear variable differential transformer (LVDT). The stylus moves over the sample surface. Surface variations cause the stylus to be translated vertically. Electrical signals corresponding to the stylus movement are produced as the core position of the LVDT changes. The LVDT scales an ac reference signal proportional to the position change, which in turn is conditioned and converted to a digital format through a high precision, integrating, analog-to-digital converter [22]. The film whose thickness has to be measured is deposited with a region masked. This creates a step on the sample surface. Then the thickness of the sample can be measured accurately by measuring the vertical motion of the stylus over the step.

2.3.2 **Surface morphology**

Surface morphology is an important property since while going for multilayer devices roughness of the thin film surface play an important role. Some of the characterization tools which clearly demonstrates an idea about the surface of the thin films is described below.
i) Scanning electron microscope (SEM)

The scanning electron microscope (SEM) is a microscope that uses electrons rather than light to form an image. There are many advantages for using the SEM instead of a light microscope [23,24]. The SEM has a large depth of field, which allows a large amount of the sample to be in focus at the same time. The SEM also produces images of high resolution, which means that closely spaced features can be examined at a high magnification. Preparation of the samples is relatively easy since most SEMs only require that sample should be conductive. The combination of higher magnification, larger depth of focus, greater resolution, and ease of sample observation makes SEM one of the most heavily used instruments in the research field. The electron beam comes from a filament, made of various types of materials. The most common is the Tungsten hairpin gun. This filament is a loop of tungsten that functions as the cathode. A voltage is applied to the loop, causing it to heat up. The anode, which is positive with respect to the filament, forms powerful attractive forces for electrons. This causes electrons to accelerate toward the anode. The anode is arranged, as an orifice through which electrons would pass down to the column where the sample is held. Other examples of filaments are lanthanum hexaboride filaments and field emission guns.

Fig: 2.3 The focusing of electrons in SEM
The streams of electrons that are attracted through the anode are made to pass through a condenser lens, and are focused to very fine point on the sample by the objective lens (figure 2.3). The electron beam hits the sample, producing secondary electrons from the sample. These electrons are collected by a secondary detector or a backscatter detector, converted to a voltage, and amplified. The amplified voltage is applied to the grid of the CRT that causes the intensity of the spot of light to change. The image consists of thousands of spots of varying intensity on the face of a CRT that correspond to the topography of the sample. In the present thesis, JEOL JSM 5600 was used for SEM analysis.

2.3.3 Average roughness with stylus profilometer:

The average roughness Ra is measured using a stylus profilometer [22] using the formula

\[ R_a = \frac{1}{L} \int_{x=0}^{x=L} h(y)dx \]

Where L is the total length of the coated film

2.3.4 Compositional analysis

In order to check the stoichiometry of the deposited films, compositional analysis is essential and the characterization tool used in the present investigation is described below.

i) Energy dispersive x-ray (EDX) analysis

EDX analysis stands for energy dispersive x-ray analysis. It is sometimes referred to also as EDS or EDAX analysis. It is a technique used for identifying the elemental composition of the specimen, on an area of interest thereof. The EDX analysis system works as an integrated feature of a scanning electron microscope (SEM), and can not operate on its own without the latter [23,24].
During EDX Analysis, the specimen is bombarded with an electron beam inside the scanning electron microscope. The bombarding electrons collide with the specimen atom’s own electrons, knocking some of them off in the process. A position vacated by an ejected inner shell electron is eventually occupied by a higher-energy electron from an outer shell. To be able to do so, however, the transferring outer electron must give up some of its energy by emitting an X-ray. The amount of energy released by the transferring electron depends on which shell it is transferring from, as well as which shell it is transferring to. Furthermore, the atom of every element releases X-rays with unique amounts of energy during the transferring process. Thus, by measuring the energy of the X-rays emitted by a specimen during electron beam bombardment, the identity of the atom from which the X-ray was emitted can be established.

The output of an EDX analysis is an EDX spectrum, which is a plot of how frequently an X-ray is received for each energy level. An EDX spectrum normally displays peaks corresponding to the energy levels for which the most X-rays had been received. Each of these peaks are unique to an atom, and therefore corresponds to a single element. The higher a peak in a spectrum, the more concentrated the element is in the specimen. An EDX spectrum plot not only identifies the element corresponding to each of its peaks, but the type of X-ray to which it corresponds as well. For example, a peak corresponding to the amount of energy possessed by X-rays emitted by an electron in the L-shell going down to the K-shell is identified as a $K_{\alpha}$ peak. The peak corresponding to X-rays emitted by M-shell electrons going to the K-shell is identified as a $K_{\beta}$ peak as shown in figure 2.4.
2.3.5 Structural characterization

i) X-ray diffraction

The structural characterization was done by recording the X-ray diffraction (XRD) pattern of the samples. XRD pattern was taken using Rigaku X-ray diffractometer with Cu-Kα radiation (λ=1.5414Å⁰). A given substance always produces a characteristic diffraction pattern whether that substance is present in the pure state or as one constituent of a mixture of substances. This fact is the basis for the diffraction method of chemical analysis. The particular advantage of X-ray diffraction analysis is that it discloses the presence of a substance, as that substance actually exists in the sample and not in terms of its constituent chemical elements. Diffraction analysis is useful whenever it is necessary to know the state of chemical combination of the elements involved or the particular phase in which they are present. Compared with ordinary chemical analysis the diffraction method has the advantage that it is usually much faster, requires only very small quantity of sample and is non destructive [25, 26].

Fig: 2.4 The emission of x rays
The basic law involved in the diffraction method of structural analysis is the Bragg’s law. When monochromatic beam of x-rays impinge upon the atoms in a crystal lattice, each atom acts as a source of scattering. The crystal acts as a series of parallel reflecting planes. The intensity of the reflected beam at certain angles will be maximum when the path difference between two reflected waves from two different crystal planes is an integral multiple of $\lambda$. This condition is termed as Bragg’s law and is given by $n \lambda = 2d \sin \theta$, where $n$ is the order of diffraction, $\lambda$ is the wavelength of X-rays, $d$ is the spacing between consecutive parallel planes and $\theta$ is the glancing angle (or the complement of the angle of incidence) [27].

X-ray diffraction studies give a whole range of information about the crystal structure, orientation, average crystalline size and stress in the powder. Experimentally obtained diffraction patterns of the sample are compared with the standard powder diffraction files published by the international centre for diffraction data (ICDD). The average grain size of the film can be calculated using the Scherrer’s formula[25]

\[
d = \frac{0.9\lambda}{\beta \cos \theta}
\]

where, $\lambda$ is the wavelength of the x-ray and $\beta$ is the full width at half maximum intensity in radians. The lattice parameter values ($a$ and $c$) for hexagonal system can be calculated from the following equations using the (hkl) parameters and the interplanar spacing $d$.

\[
\frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2+hk+k^2}{a^2} \right) + \frac{l^2}{c^2}
\]
X-ray diffraction measurements of the films in the present studies were done using Rigaku automated X-ray diffractometer. The filtered copper Kα ($\lambda = 1.5414\text{Å}$) radiation was used for recording the diffraction pattern.

2.3.6 Measurement of contact angles

The contact angle is defined as the angle made by the intersection of the liquid/solid interface and the liquid/air interface. It can be alternately described as the angle between solid sample’s surface and the tangent of the droplet’s ovate shape at the edge of the droplet. A high contact angle indicates a low solid surface energy or chemical affinity [28, 29, 30]. This is also referred to as a low degree of wetting. A low contact angle indicates a high solid surface energy or chemical affinity, and a high or sometimes complete degree of wetting. The three degrees of wetting are shown in fig 2.5. For example, a contact angle of zero degrees will occur when the droplet has turned into a flat puddle; this is called complete wetting. Young proposed that the contact angle represents the vectorial balance of three tensors, the surface tension of the solid in air, the surface tension of the liquid in equilibrium with the vapour and the interfacial tension between the solid and the liquid. The solid-vapor interfacial energy is denoted as $\gamma_{SV}$, the solid-liquid interfacial energy as $\gamma_{SL}$ and the liquid-vapor energy as simply $\gamma$, we can write an equation that must be satisfied in equilibrium (known as the Young’s Equation 2.5):

$$0 = \gamma_{SV} - \gamma_{SL} - \gamma \cos \theta_C \quad \text{------------------- (2.5)}$$

where $\theta_C$ is the equilibrium contact angle.

The simplest way of measuring the contact angle is with a goniometer shown in fig 2.6 using the static sessile drop method [30], which allows the user to measure the contact angle visually. When a drop of liquid is placed on a surface of a solid that is smooth, planar, and level, the liquid either spreads out
to a thin surface film, or it forms a sessile droplet on the surface. The droplet has a finite between the solid and the liquid and the surface tension of the liquid. The contact angle equilibrium has received a great deal of attention, principally because it is perhaps the simplest direct experimental approach to the thermodynamic work of adhesion. The droplet is deposited by a syringe pointed vertically down onto the sample surface, and a high resolution camera captures the image, which can then be analyzed either by eye (with a protractor) or using image analysis software. The size of the droplet can be increased gradually so that it grows proportionally, and the contact angle remains congruent. By taking pictures incrementally as the droplet grows, the user can acquire a set of data to get a good average. If necessary, the receding contact angle can also be measured by depositing a droplet via syringe and recording images of the droplet being gradually sucked back up.

**Fig 2.5** A sketch of three degrees of wetting and the corresponding contact angles
An alternative method for measuring the contact angle is the Whilemy method, which employs a sensitive force meter of some sort to measure a force that can be translated into a value of the contact angle. In this method, a small plate-shaped sample of the solid in question, attached to the arm of a force meter, is vertically dipped into a pool of the probe liquid (in actuality, the design of a stationary force meter would have the liquid being brought up, rather than the sample being brought down), and the force exerted on the sample by the liquid is measured by the force meter. This force is related to the contact angle by the equation 2.6:

$$ F = F_b + \frac{\pi \rho L \sigma}{2} $$

Where $F$ is the total force measured by the force meter, $F_b$ is the force of buoyancy due to the solid sample displacing the liquid, $L$ is the wetted length, and $\sigma$ is the known surface tension of the liquid. The contact angles of the samples with three different fluids were measured using a contact angle goniometer (NRL) using the sessile drop method [30] in three well characterized liquids, water, formamide and di-iodomethane as per previous studies.
2.3.7 Hardness testing

Hardness is the ability of a material to resist permanent indentation or deformation when in contact with an indenter under load. Generally a hardness test consists of pressing an indenter of known geometry and mechanical properties into the test material. The hardness of the material is quantified using one of a variety of scales that directly or indirectly indicate the contact pressure involved in deforming the test surface[31,32]. Since the indenter is pressed into the material during testing, hardness is also viewed as the ability of a material to resist compressive loads. The indenter may be spherical (Brinell test), pyramidal (Vickers and Knoop tests), or conical (Rockwell test). In the Brinell, Vickers and Knoop tests, hardness value is the load supported by unit area of the indentation. In the Rockwell tests, the depth of indentation at a prescribed load is determined and converted to a hardness number (without measurement units), which is inversely related to the depth. In microindentation hardness testing, a diamond indenter of specific geometry is impressed into the surface of the test specimen using a known applied force.

**Vickers Hardness Test.** This indentation test employs a square-based pyramidal-shaped indenter made from diamond. Fig 2.7 shows examples of Vickers indents to illustrate the influence of test force on indent size.
Fig. 2.7 Vickers hardness test. (a) Schematic of the square-based diamond pyramidal indenter used for the Vickers test and an example of the indentation it produces. (b) Vickers indents made in ferrite in a ferritic-martensitic high-carbon version of 430 stainless steel using (left to right) 500, 300, 100, 50, and 10gf test forces (differential interference contrast illumination, aqueous 60% nitric acid, 1.5 V dc). 250× Magnification

In this test, the force is applied smoothly, without impact, and held in contact for 10 to 15 s. The force must be known precisely (refer to ASTM E 384 for tolerances). After the force is removed, both diagonals are measured and the average is used to calculate the HV according to equation 2.7:

\[
HV = \frac{200P\sin(\frac{\alpha}{2})}{d^2} = \frac{1854.4P}{d^2} \quad \text{(2.7)}
\]

where \(d\) is the mean diagonal in \(\mu\text{m}\), \(P\) is the applied load in gf, and \(\alpha\) is the face angle.

2.3.8 Microscratch adhesion testing

One of the primary requirements of a PVD coating is excellent adhesion of the coating to the substrate, a property that can be defined as the interfacial forces between two surfaces. The most common method of assessing PVD coating adhesion is the scratch tester [33, 34, 35]. The scratch tester moves a Rockwell diamond tip with a radius of 200µm across the coated surface of a
substrate at a constant velocity while an increasing normal force is applied with a constant loading rate. The scratch test introduces stresses to the interface between coating and substrate causing delamination or chipping of the coating. The critical normal force at which the first failure of the coating is detected is termed the critical load $L_c$.

**Fig 2.8 Set up of a scratch test procedure**

The typical scratch tester has three methods of detecting coating failure; a load cell to measure the change in friction, acoustic emission or observation of the scratch channel using an attached optical microscope. The best scratch adhesion testers use all three methods of coating failure detection. The intensity of the acoustic emission is dependent on the type of coating failure during the adhesion test e.g. cracking, chipping (cohesive failure) and delamination (adhesive failure). It is therefore important to observe the coating failure after
the adhesion test using an optical microscope to confirm the critical load. Figure 2.7 shows a set up for the scratch test.

In this work the change of frictional coefficient was measured to assess the adhesion strength of HA on Ti. The normal and tangential forces were continuously acquired using a computer with data acquisition electronics. The tests were conducted under ambient conditions of 28°C and Relative humidity of 40%. The coefficient of friction was calculated using the formula given by Eq. 2.8

\[ \mu = \frac{T}{N} = \frac{FT \cos \theta - FN \sin \theta}{FT \sin \theta + FN \cos \theta} \]

where ‘\( \theta \)’ is the angle of inclination of the sample, \( FT \) the recorded traction force and \( FN \) the recorded normal force at any instance.

### 2.3.9 Thermogravimetric analysis

Thermogravimetric analysis (TGA) is an analytical technique used to determine a material’s thermal stability and its fraction of volatile components by monitoring the weight change that occurs as a specimen is heated [36, 37]. The measurement is normally carried out in air or in an inert atmosphere, such as Helium or Argon, and the weight is recorded as a function of increasing temperature. Sometimes, the measurement is performed in a lean oxygen atmosphere (1 to 5% \( O_2 \) in \( N_2 \) or He) to slow down oxidation. In addition to weight changes, some instruments also record the temperature difference between the specimen and one or more reference pans (differential thermal analysis, or DTA) or the heat flow into the specimen pan compared to that of the reference pan (differential scanning calorimetry, or DSC). The latter can be used to monitor the energy released or absorbed via chemical reactions during the heating process.
Analysis is carried out by raising the temperature gradually and plotting weight against temperature. The temperature in many testing methods routinely reaches 1000°C or greater, but the oven is so greatly insulated that an operator would not be aware of any change in temperature even if standing directly in front of the device. After the data is obtained, curve smoothing and other operations may be done such as to find the exact points of inflection. In this study TGA was conducted on HA to assess its water loss temperature.
References


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