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Thin Film Coatings for Biomaterials and Biomedical Applications

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Contents

List of contributors	ix
Woodhead Publishing Series in Biomaterials	xi
Part One Fundamentals of thin film technologies for biomedical applications	1
1 Thin film deposition technologies and processing of biomaterials	3
<i>P.H. Li, P.K. Chu</i>	
1.1 Introduction	3
1.2 Chemical vapor deposition	3
1.3 Physical vapor deposition	9
1.4 Electrophoretic deposition	16
1.5 Sol-gel method	19
1.6 Spraying processes	19
1.7 Conclusion	22
References	22
2 Thin film growth on biomaterial surfaces	29
<i>A. Michelmore</i>	
2.1 Introduction	29
2.2 Some examples of applications	30
2.3 Materials and technologies	31
2.4 Mechanisms of deposition	35
2.5 Monitoring thin film growth	37
2.6 Challenges and future trends	42
2.7 Further reading	42
References	43
3 Tailoring thin films for implant-specific applications	49
<i>T.W.J. Steele, J.S.C. Loo, S.S. Venkatraman</i>	
3.1 Introduction	49
3.2 Materials and technologies	49
3.3 Challenges and examples	53
3.4 Future trends	57
References	59

4	Protein and peptide interactions with phospholipid membranes and surfaces	61
	<i>M. Malmsten</i>	
4.1	Introduction	61
4.2	Protein interactions with phospholipid membranes and surfaces	62
4.3	Peptide interactions with phospholipid membranes and surfaces	64
4.4	Phospholipid-mimicking polymers	72
4.5	Future trends	72
	Acknowledgments	74
	References	74
 Part Two Properties of thin films for biomedical applications		 79
5	Characterization of thin films for biomedical applications	81
	<i>N.S. Murthy, V.B. Damodaran, S.H. Lee, A.S. Hwang, H.-J. Sung</i>	
5.1	Introduction	81
5.2	Physical characterization	82
5.3	Chemical characterization	92
5.4	Characterization of initial biological interactions	102
5.5	Concluding remarks	108
	References	109
6	Mechanical behavior and properties of thin films for biomedical applications	117
	<i>A.H. Choi, B. Ben-Nissan, A. Bendavid, B. Latella</i>	
6.1	Introduction	117
6.2	Stresses in thin films	118
6.3	Adhesion of thin films	119
6.4	Mechanical and adhesion testing methods of thin films	121
6.5	Adhesion and mechanical properties of thin films: examples	129
6.6	Finite element examination of thin films	130
6.7	Concluding remarks	135
	References	136
7	Thin film coatings and the biological interface	143
	<i>J. Chen</i>	
7.1	Introduction	143
7.2	Materials and technologies	144
7.3	Cell–material interactions	145
7.4	Primitive examples	146
7.5	Challenges and future trends	152
	Acknowledgements	153
	References	153

Part Three	Functional thin films for biomedical applications	165
8	Thin films for tissue engineering applications	167
	<i>M. Mozafari, A. Ramedani, Y.N. Zhang, D.K. Mills</i>	
8.1	Introduction	167
8.2	Thin film coating technologies for tissue engineering applications	168
8.3	Novel innovative strategies for tissue engineering purposes	187
8.4	Conclusion	188
	References	189
9	Thin film coatings for stem cell technologies	197
	<i>T. Fernandez, N. Rogers, J.D. Whittle</i>	
9.1	Introduction	197
9.2	Thin film coatings for culture of normal cells	197
9.3	Thin film coatings for culture of stem cells	207
9.4	Challenges	210
9.5	Understanding stem cell interactions with extracellular matrix molecules	210
9.6	Surface treatments to enhance biocompatibility for stem cell culture	211
9.7	Future trends	213
	References	214
10	Uniform, adhesive, and low cytotoxic films accelerating bacterial reduction in the dark and under visible light	225
	<i>S. Rtimi, C. Pulgarin, J. Kiwi</i>	
10.1	Introduction	225
10.2	Results and discussion: design, magnetron sputtering, evaluation of bacterial reduction, and surface layer characterization	228
10.3	Conclusions and future outlook	255
	Acknowledgments	256
	References	256
11	DLC thin films for implantable medical devices	261
	<i>T.I.T. Okpalugo, A.A. Ogwu</i>	
11.1	Introduction	261
11.2	Materials and technologies	261
11.3	Major challenges to using diamond-like carbon for implantable medical devices: cellular and blood interactions	262
11.4	Examples	281
11.5	Future trends	282
	References	283
Index		289

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Thin film deposition technologies and processing of biomaterials

1

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1.1 Introduction

On the heels of continuous biomedical and clinical research and development, high demand is placed on the processing and engineering of biomaterials. Besides the rigorous selection of materials based on their bulk properties, the surface properties of biomaterials are crucial to clinical success. Compared with the development of new biomaterials, modification of selected surface biological and mechanical properties of existing biomaterials to cater to specific needs and applications tends to be more economical and less time-consuming. In particular, deposition of thin films or coatings is a common and effective technique in surface modification and engineering. Methods for thin film deposition can be divided into two groups based on the nature of the deposition process, chemical or physical. Basically, chemical methods such as chemical vapor deposition (CVD) and sol-gel involve gas-phase or liquid-phase chemical reactions whereas physical methods typically include evaporation, sputtering (ejection of materials from a target followed by condensation to form films), and spraying. This chapter presents an overview of the fundamentals of thin film deposition and pertinent instrumentation with an emphasis on applications to biomaterials.

1.2 Chemical vapor deposition

1.2.1 *Plasma-enhanced chemical vapor deposition*

CVD is a well-understood thin film deposition method that uses chemical reactions of vapor-phase precursors. CVD processes have traditionally been initiated and controlled by heat as the source of energy. An elevated deposition temperature is normally required, which restricts the types of substrates that can be used and coating materials that can be deposited, especially thermally sensitive ones (Jones and Hitchman, 2009). However, thermal energy is not the only energy supplied to the system; plasmas and photons are widely used in CVD processes. Plasma-enhanced chemical vapor deposition (PECVD), or plasma-assisted CVD, is a CVD technique in which plasma in lieu of thermal energy is used primarily to activate ions and radicals in the chemical reactions leading to layer formation on the substrate. One major advantage of PECVD over

conventional thermal CVD is that the lower temperature in PECVD allows the deposition of layers that cannot tolerate a high temperature, and temperature-sensitive substrates can be used. Moreover, the deposition rate in PECVD is typically higher and more easily controlled because the precursors activated by the plasma are more reactive and a biased voltage can be applied to control the arrival rate of the ionized precursors (Chu et al., 2004).

The plasma in PECVD is usually triggered and sustained by radio frequency (RF), microwave (MW), and a combination of these. RF PECVD systems use either internal electrodes or external plasma excitation employing a coil or rings, as illustrated in Fig. 1.1(a) and (b). The frequency used in RF PECVD is commonly between 50 kHz and 13.56 MHz, and operation pressure is between 0.1 and 2.0 Torr. Plasma density is typically between 10^8 and 10^{12} cm^{-3} , and the fastest electrons may possess energy as high as 10–30 eV (Kern, 1991; Chu et al., 2004). MW discharge (Fig. 1.1(c)) typically takes place at a MW frequency of 2.54 GHz. Plasma density in the surface wave discharge can be as low as 10^8 cm^{-3} in the low-pressure and low-frequency range and can be as large as 10^{15} cm^{-3} at atmospheric pressure (Anders, 2000; Chu et al., 2004). There are also dual-mode PECVD systems that apply RF-biased voltage to the substrate holder (Fig. 1.1(d) and (e)).

PECVD has been used industrially for several decades to deposit oxides and nitrides of silicon, polycrystalline silicon, and epitaxial silicon (Tedrow and Reif, 1994) for microelectronics. There are also many applications in the automotive,

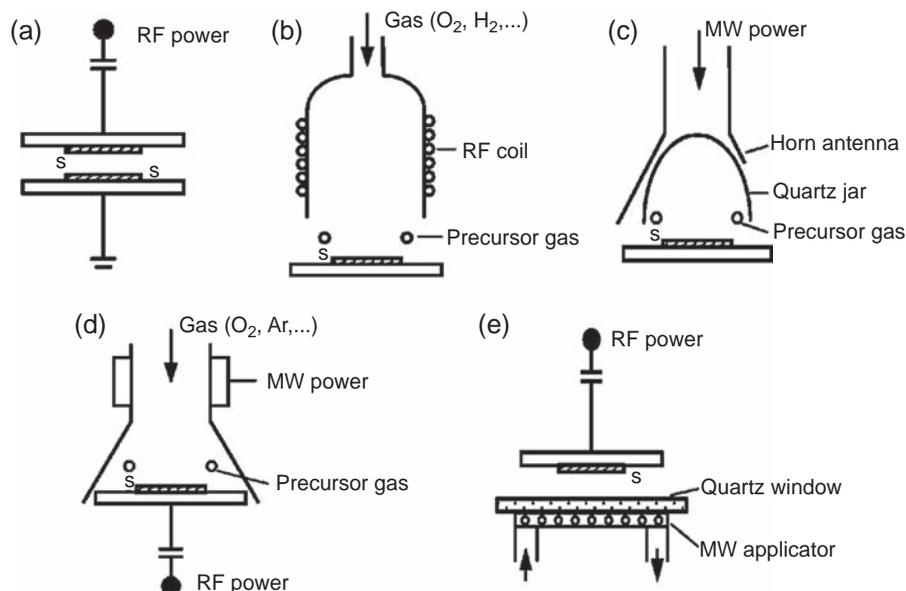


Figure 1.1 Typical PECVD reactor systems: (a) parallel plate RF PECVD; (b) remote RF PECVD; (c) MW PECVD; (d) remote MW/RF PECVD; (e) dual-mode MW/RF PECVD. Reprinted with permission from Martinu, L., Poitras, D., 2000. Plasma deposition of optical films and coatings: a review. *J. Vac. Sci. Technol. A Vac. Surf. Films* 18, 2619–2645.

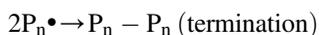
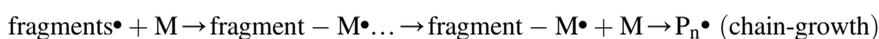
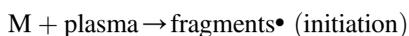
biomedical, and manufacturing fields (Martinu et al., 2009). Here, the deposition of inorganic or metallic films by PECVD for biomaterials applications is discussed. The PECVD process of polymer films or coatings with organic precursors, termed plasma polymerization, will be discussed in Section 1.2.2.

PECVD films have received much attention in the biomedical field, especially silicon-based films such as amorphous silicon (Persheyev et al., 2011), silicon carbide (Bolz and Schaldach, 1990; Daves et al., 2011), and silicon nitride (Wei et al., 2008; Wan et al., 2005). Owing to the wide use of silane (SiH_4), these films are typically hydrogenated; for instance, a-Si:H, a-SiC:H, and a-SiN:H. Liu et al. (2007) fabricated hydrogenated amorphous silicon (a-Si:H) films on silicon by PECVD and examined the formation of hydroxyapatite on the surface. The presence of surface Si–H bonds is believed to induce apatite formation, and surface bioactivity is crucial to the development of bioactive silicon-based implants. $\text{SiN}_x\text{:H}$ films with different N/Si ratios have been synthesized and their surface hemocompatibility has been investigated. Improved hemocompatibility is observed in $\text{SiN}_x\text{:H}$ films compared with low-temperature isotropic carbon (LTI-C), and films with more Si–N bonds show less platelet activation, which makes them potentially more blood-compatible than LTI-C and $\text{SiN}_x\text{:H}$ films with fewer Si–N bonds (Wan et al., 2005). Carbon-based films such as diamond-like carbon (DLC) and carbon nitride deposited by PECVD are attracting increasing interest as biomaterials. DLC films are deposited onto silicon by PECVD with methane (CH_4) as the precursor; osteoblast adhesion and proliferation tests conducted in vitro reveal that the DLC coating has better surface stability and exhibits improved cellular response (Chai et al., 2008). Ahmed et al. (2012) incorporated fluorine into DLC using acetylene (C_2H_2) and carbon tetrafluoride (CF_4) to control protein adsorption. Their results indicate that adsorption of amino acids is enhanced at low fluorine doping, but a larger fluorine concentration results in reduced adsorption compared with undoped DLC. Fluorine doping of DLC is thus a feasible approach to tailor protein adsorption.

1.2.2 Plasma polymerization

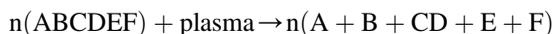
Plasma polymerization, or glow discharge polymerization (Yasuda, 1981), is the process of forming plasma-polymerized thin films based on PECVD using organic or organometallic precursors. Briefly, plasma polymerization involves the fragmentation and subsequent deposition of organic precursors or monomers (Siow et al., 2006). The organic monomer gas is fed into the reaction chamber alone or combined with a carrier gas such as argon or helium, forming the plasma and recombining on the substrate to realize film deposition (Förch et al., 2005). Plasma chemistry is normally complex and nonspecific in nature, and so plasma polymerization cannot be explicated without considering the fragmentation of molecules in both the gas and solid phases. That is, the reactive species in the plasma phase do not all originate from the monomer gas, but may be mixed with reactive species from competitive ablation of the already deposited materials. The polymerization and ablation mechanisms occur simultaneously on the substrate; these complicated processes have been described by Yasuda as competitive ablation polymerization (Yasuda and Yasuda, 2000).

The chemical reactions leading to polymer fabrication in plasma polymerization are generally complex, and the mechanisms of plasma polymerization have been extensively studied but are also controversial. Friedrich (2011) reviewed the mechanism from a chemical point of view and concluded that there are two predominant mechanisms: plasma-induced radical chain-growth polymerization and atomic fragmentation–recombination. Plasma-induced radical chain-growth polymerization is similar to classical radical polymerization involving initiation, chain-growth, and termination processes. Radicals or radical fragments (fragments•) are produced in the plasma and initiate the reaction. The polymer chain grows by addition of monomer molecules (M) and chain growth is predominately terminated by radical recombination, thus forming a polymer:



Plasma-induced ionic chain-growth polymerization may also occur similar to that of radicals: $\text{fragment}^+ + M \rightarrow P_n^+$, $P_n^+ + M \rightarrow P_{n+1}^+$.

The monomer molecules are extensively fragmented into single atoms or atomic fragments in high-power plasma. The polymerization process obeys the atomic fragmentation–recombination mechanism. The atoms and fragments bombard the substrate surface, forming plasma polymers with a high degree of irregularity by random recombination (Friedrich, 2011):



The mechanism differs greatly from conventional polymerization. Plasma polymers do not contain chains with regular repeating units, but tend to form a branched or cross-linked network. Thus, plasma polymers can have exceptional mechanical properties and good adhesion to most substrates (Stamm, 2008). Monomers in plasma polymerization are not restricted to unsaturated organics used in conventional polymerization and can be unpolymerizable saturated organic molecules. The diversity of organic monomers makes plasma polymerization a versatile tool for the deposition of polymeric thin films in a variety of applications.

The biomedical application of plasma polymerization mainly relies on changing the surface chemistry and tailoring the surface to be either bioreactive or nonreactive (Förch et al., 2007). Plasma polymerization can be implemented with a high retention of functional groups from the organic monomers. Amine or carboxyl groups are of particular interest to form a bioreactive surface to effect the binding of biomolecules and the adhesion of cells (Carton et al., 2012; Yang et al., 2014; Zhao et al., 2011). Finke et al. (2007) coated a very thin, adherent, cross-linked, pinhole- and additive-free allylamine plasma polymer layer (PPAAm) on polished

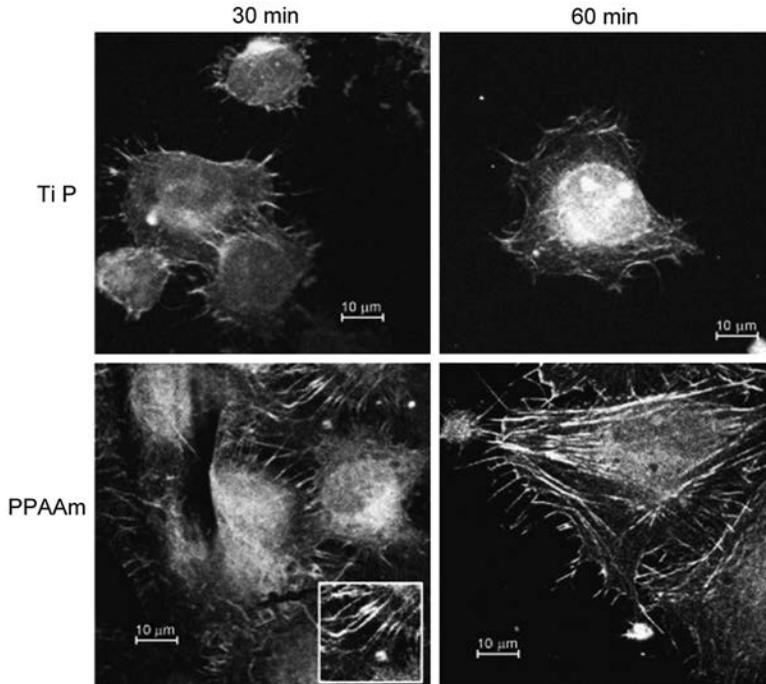


Figure 1.2 Time-dependent actin development in MG-63 osteoblasts.

Reprinted with permission from Finke, B., Luethen, F., Schroeder, K., Mueller, P.D., Bergemann, C., Frant, M., Ohl, A., Nebe, B.J., 2007. The effect of positively charged plasma polymerization on initial osteoblastic focal adhesion on titanium surfaces. *Biomaterials* 28, 4521–4534.

titanium. Time-dependent actin development of human MG-63 osteoblast cells after short attachment for 30 and 60 min was pronounced on the PPAAm surface (Fig. 1.2), indicating enhanced initial osteoblastic focal adhesion formation. In addition to the interactive surface, sometimes antifouling surfaces with bio-nonreactive properties are needed to prevent adhesion of proteins, platelets, or any other biological entities. Plasma polymers with polyethylene glycol-like groups or similar structures rich in ether functional groups have particular protein resistance properties. Plasma-polymerized fluorinated coatings are good candidates for bio-nonreactive surfaces (Kumar et al., 2010; Favia, 2012).

1.2.3 Atomic layer deposition

Atomic layer deposition (ALD), originally termed atomic layer epitaxy, was pioneered and patented by T. Suntola and coworkers for growing ZnS (Suntola and Antson, 1977). Initial motivation for the development of ALD came from thin film electroluminescent displays. After extensive research advances in the past 40 years, ALD, which allows deposition at the atomic or molecular level, can be used for a variety of thin films such as metal oxides and nitrides, polymers, and inorganic–organic

hybrid materials with control at the atomic or molecular level (George, 2010). This versatile technique has been adopted by the microelectronics industry but is also used to produce plasmonics materials, medical devices, and biomaterials (Im et al., 2012; Knez et al., 2007; Skoog et al., 2013).

ALD is conducted in cycles. In one cycle, alternating chemical reactions of two precursors, “a” and “b,” occur with purging with an inert gas in between. Precursor “a” is first saturated and chemisorbed on the surface of the substrate. After excessive precursor “a” in the gas phase is removed by purging with the inert gas, the precursor gas “b” then reacts with the chemisorbed precursor “a” on the substrate, producing a layer of the desired materials. The excess precursor “b” and by-products are removed by a second purging and the growth cycle is repeated until the desired film thickness is obtained. As an example, the growth cycle to deposit a TiO_2 thin film employing gaseous precursors TiCl_4 and H_2O is presented in Fig. 1.3. The sequential and saturating surface reactions ensure self-limitation of the film growth. Thus, the film thickness depends only on the number of reactions cycles, thereby enabling precise and simple control of the thickness. The small deposition rate in ALD is also desirable in some applications (Ritala and Niinisto, 2009).

Thin films prepared by ALD possess biologically relevant surface properties enabling many biomedical applications. For instance, hard CrN coatings on steel have been sealed with 50-nm-thick $\text{Al}_2\text{O}_3\text{--Ta}_2\text{O}_5$ nano-laminates prepared by ALD (Härkönen et al., 2014). The ALD layer smoothes the CrN surface because it

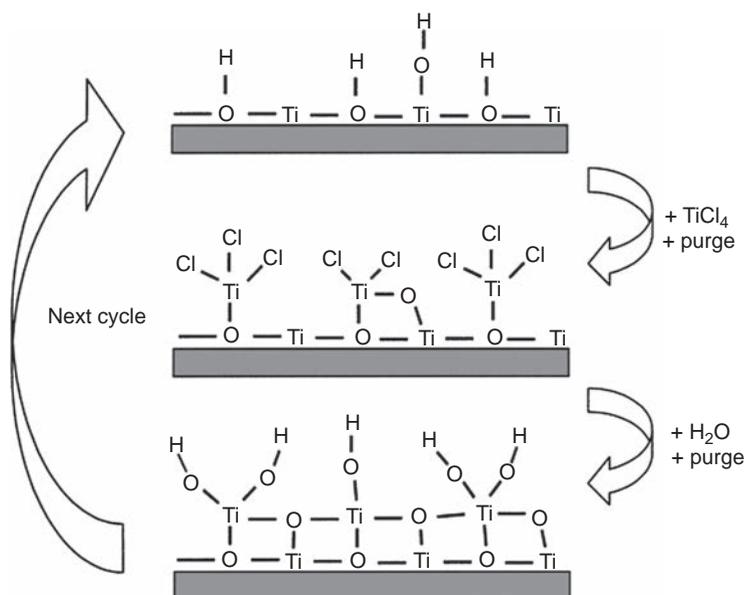


Figure 1.3 Schematic illustration of ALD deposition of TiO_2 films using TiCl_4 and H_2O . Reprinted with permission from Leskelä, M., Ritala, M., 2003. Atomic layer deposition chemistry: recent developments and future challenges. *Angew. Chem.* 42, 5548–5554.

penetrates the pinhole defects. Effective sealing by ALD improves corrosion protection of the CrN coatings. Slaney et al. (2011) used ALD to produce a 15-nm-thick conformal silica film with superior electrochemical properties. Trialkoxysilane derivatives of two monosaccharides are then attached to the hydroxyl groups of silica, enabling straightforward functionalization of the silica-coated stainless-steel surface. The presence and biological function of the monosaccharides on the functionalized surfaces are confirmed by an enzyme-linked lectin assay, which suggests that ALD can functionalize stainless-steel stents and other implants. Putkonen et al. (2009) conducted ALD to prepare hydroxyapatite on Si (100) and Corning (0211) substrates. Postdeposition annealing at 500°C produces partially crystalline hydroxyapatite films and the degree of crystallinity increases with annealing temperature. In vitro studies reveal that mouse MC3T3-E1 osteoblast cells attach better on the annealed hydroxyapatite surface and indicate that the ALD-deposited hydroxyapatite film has enhanced biocompatibility.

Compared with conventional CVD methods, the saturation/reaction/purging cycles in ALD allow the longer lifetime of the precursor molecules to transport and diffuse to the cavities in complicated three-dimensional substrates. As a result, one can expect better uniformity and conformity on complex substrates for ALD compared with conventional CVD (Lee et al., 2011). Hence, ALD is practical for substrates with a complex surface morphology. Hyde et al. (2009) deposited conformal and uniform TiNO_x films on cellulose fiber substrates at 100°C. In vitro studies involving human adipose-derived adult stem cells are carried out on films with different thicknesses. The 20-Å-thick TiNO_x film has the largest amount of adhered cells, and by altering the film thickness it is possible to control the quantities of adhered cells. The results suggest that ALD is useful in the surface modification of biocompatible implant materials. Skoog et al. (2012) used ALD to produce nanoporous alumina membranes with zinc oxide. In vitro agar diffusion assays show that zinc oxide-coated nanoporous alumina membranes inhibit the growth of several bacteria found on skin, including *Bacillus subtilis*, *Escherichia coli*, *Staphylococcus aureus*, and *Staphylococcus epidermidis*. Im et al. (2010) deposited thin alumina dielectric layers by ALD to form vertical nanogap structures for surface-enhanced Raman scattering (SERS) (Fig. 1.4). By decreasing the gap size to 5 nm, local SERS enhancement of up to 10⁹ can be accomplished. With state-of-the-art ALD protocols, it is possible to push the limits of this scheme to make well-defined 1- to 2-nm nanogaps, and the technique can be applied to nonlinear optics and biosensing.

1.3 Physical vapor deposition

1.3.1 Evaporation

Evaporation, or vacuum deposition, is a simple physical vapor deposition (PVD) process in which atoms or molecules are evaporated from the source thermally, travel without collisions with residual gas molecules in the deposition chamber, and condense on the substrate. Two heating mechanisms are commonly used in

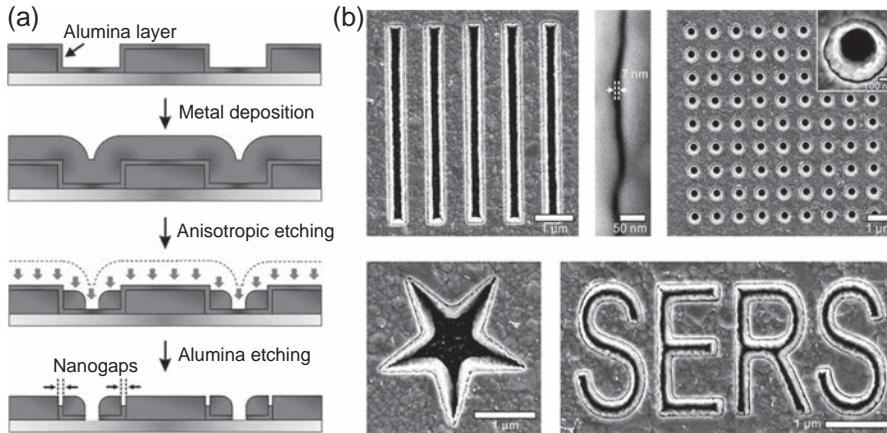


Figure 1.4 (a) Schematic showing the fabrication process of nanogap arrays using ALD. The nanogap size is determined by the thickness of the alumina layer. (b) Scanning electron microscopy images of various nanogap structures.

Reprinted with permission from Im, H., Bantz, K.C., Lindquist, N.C., Haynes, C.L., Oh, S.-H., 2010. Vertically oriented sub-10-nm plasmonic nanogap arrays. *Nano Lett.* 10, 2231–2236.

evaporation: resistive heating and electron beam heating, as illustrated in Fig. 1.5. In resistive heating, the materials in a boat of crucible are evaporated by heating with a filament. Common materials are W, Ta, Mo, C, and BN/TiB₂ composite ceramics. Resistive heating is the most common technique to vaporize materials at temperatures below about 1500°C (Mattox, 2010; Adachi and Wasa, 2012). In comparison, high-energy electron beams are used (commonly referred to as e-beam heating) for refractory materials. The electron beam from an e-beam gun is accelerated to a high voltage (10–20 kV),

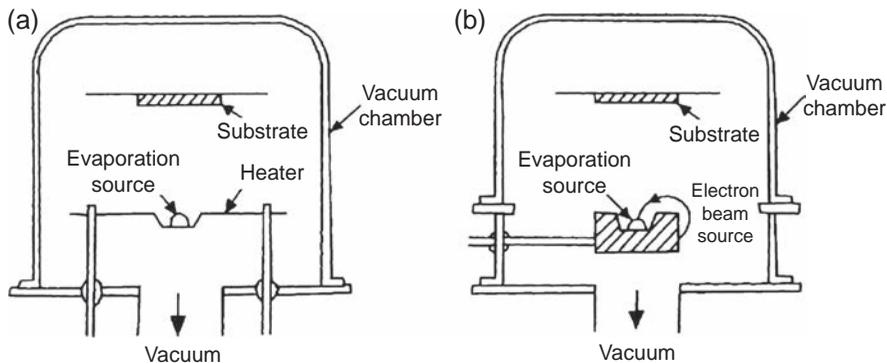


Figure 1.5 (a) Typical thermal evaporation system and (b) electron beam evaporation system. Reprinted with permission from Adachi, H., Wasa, K., 2012. *Thin films and nanomaterials*. In: Wasa, K., Kanno, I., Kotera, H. (Eds.), *Handbook of Sputtering Technology*, second ed. William Andrew Publishing, Oxford, pp. 3–39.

electrostatically or magnetically collimated and focused, and impinged onto the surface of the materials to be evaporated (Mattox, 2010). One advantage of e-beam evaporation over resistive heating is that the energy is transferred as heat only to melt the source locally instead of the entire crucible, and consequently there is less contamination from the crucible.

The evaporation process requires a relatively good vacuum to ensure collision-less trajectories of evaporated atoms before condensation. Evaporation is normally carried out in a vacuum more than 10^{-5} Torr. To minimize residual gases that can contaminate the film, a high (10^{-7} Torr) or ultrahigh ($<10^{-9}$ Torr) vacuum may be needed to produce films with the desired purity (Hung et al., 1992). The pumping system is usually based on a diffusion pump with a liquid nitrogen-cooled antireep-type baffle backed by a mechanical pump or a Roots blower/mechanical pump combination in large systems. For high-purity film deposition in which a base pressure of 10^{-9} to 10^{-10} Torr is needed, ion pumps backed by cryosorption pumps are commonly used (Martin, 2009).

Evaporation is widely used for a variety of materials including metals, elemental semiconductors, alloys, intermetallic compounds, and refractory compounds (oxides, carbides, nitrides, borides, etc.). Shah et al. (2010) reviewed materials deposited by evaporation as well as different evaporation processes such as multiple-source evaporation, reactive evaporation, and activated reactive evaporation. For instance, evaporated films of titanium (Ti), titanium oxide (TiO_2), and calcium phosphate are commonly used to tailor surface chemistry and topography for a better biological response (Hacking et al., 2007; Han et al., 2010; Chen et al., 2010). Han et al. (2010) deposited a pure titanium (Ti) layer on polyetheretherketone (PEEK) to enhance biocompatibility and adhesion to bone tissues. The Ti layer adheres firmly to the substrate and enhances wettability. The initial cell adhesion images shown in Fig. 1.6(c) and (d) indicate better cell attachment and biocompatibility. In vivo animal tests show that the Ti-coated PEEK implants have a larger bone-in-contact ratio than pure PEEK implants. Lin et al. (2009) deposited titanium oxide films by electron beam evaporation. The surface contact angle decreased and biological tests revealed substantial cell adhesion and little platelet adhesion, indicating that the e-beam-deposited Ti has good potential in cardiovascular stents.

1.3.2 Sputtering deposition

Sputtering refers to the basic and well-known process involving backward scattering of the solid surface atoms to the surface upon bombardment by energetic ions, as illustrated in Fig. 1.7 (Rautray et al., 2011). Sputtering is an etching process suitable for surface cleaning, micromachining, depth profiling, and so on. Deposition of the ejected vapor products, known as sputtering deposition, is a common film deposition technique.

Although the deposition rate is typically smaller than that of evaporation, sputtering deposition possesses several advantages compared with other PVD methods. In the sputtering system, sputtered species are generally composed of neutrals of the target materials with only a small fraction of ions when the target is bombarded ions with energies of several hundreds to thousands of electron volts. Clusters of atoms may be formed as well (Wasa, 2012a). Deposition of films by sputtering is predictable

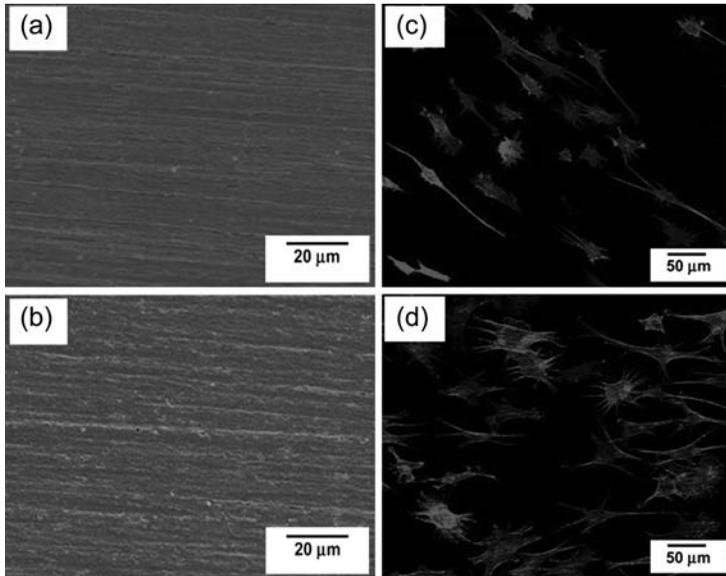


Figure 1.6 Scanning electron microscopy images of the surface of (a) as-machined and (b) Ti-coated PEEK. Confocal laser scanning microscopy images of MC3T3-E1 cells cultured on (c) as-machined and (d) Ti-coated PEEK for 3 h.

Reprinted with permission from Han, C.-M., Lee, E.-J., Kim, H.-E., Koh, Y.-H., Kim, K.N., Ha, Y., Kuh, S.-U., 2010. The electron beam deposition of titanium on polyetheretherketone (PEEK) and the resulting enhanced biological properties. *Biomaterials* 31, 3465–3470.

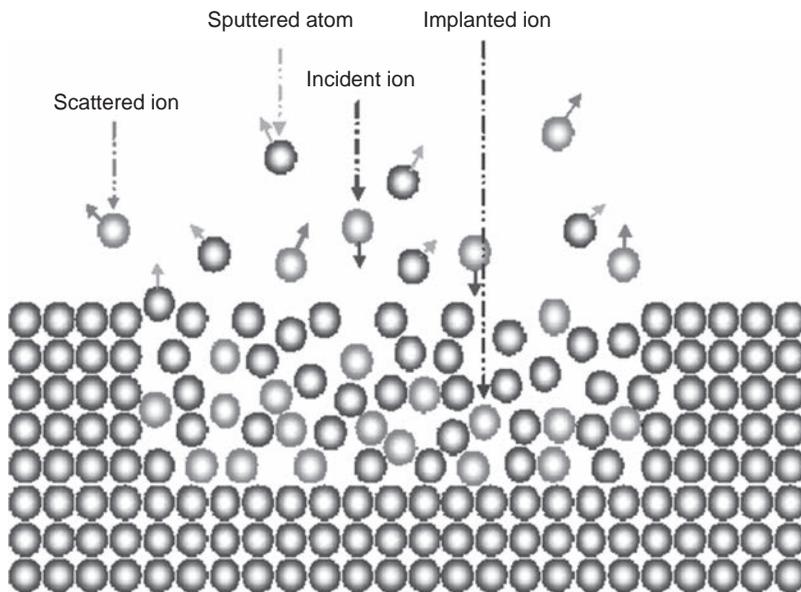


Figure 1.7 Illustration of various processes in ion–solid interactions.

Reprinted with permission from Rautray, T.R., Narayanan, R., Kim, K.-H., 2011. Ion implantation of titanium based biomaterials. *Prog. Mater. Sci.* 56, 1137–1177.

and stable. The energy distribution of the sputtered species usually has a maximum of about 4–7 eV with a long tail of over 50 eV. These energies are more than an order of magnitude higher than those of the evaporated species and allow the depositing species to penetrate more deeply into the substrate and enhance the surface mobility to form dense, well-bonded films (Suryanarayana, 1999). Moreover, sputtering is essentially a kinetic process involving momentum transfer in lieu of chemical and/or thermal processes; therefore, virtually any materials can be introduced into a gas phase by sputtered a solid target (Kern, 1991).

There are two primary ways to generate energetic ions by sputtering by means of a plasma and ion beam; common sputtering systems adopt a DC diode, RF diode, magnetron diode, and ion beam sputtering (Seshan, 2002; Wasa, 2012b). Typical systems are depicted in Fig. 1.8. DC diode sputtering constitutes a simplest sputtering system in which two planar electrodes are positioned opposite each other in a vacuum chamber. The chamber is filled with a noble gas, typically argon at 1–5 Pa. When high voltage in the range of 2000 V is applied between the cathode and anode, a glow discharge is ignited. Argon ions in the glow discharge are accelerated and sputter the cathode target, resulting in the deposition of materials sputtered from the target onto the substrate. Diode plasma cannot be operated on insulators because the sputtering discharge cannot be sustained owing to the immediate buildup of surface-positive charges on the front side of the insulators. Hence, RF-diode sputtering is commonly used to sputter insulators. The difference is that the power supply is at a high frequency, commonly 13.56 MHz. In addition to the ability to sputter insulators, the RF in the discharge chamber increases the collision probability between secondary electrons and gas molecules, thereby producing higher plasma density, larger ion currents, and faster sputtering than the DC process (Wasa, 2012b).

Magnetron sputtering is a promising low-pressure method used in most sputtering applications. Two common types of magnetron sputtering systems, cylindrical and planar, are shown in Fig. 1.8. The magnetic field is located parallel to the cathode surface, and electrons in the glow discharge experience the $E \times B$ (E cross B) drift, in which E and B denote the electric field in the discharge and superposed transverse magnetic field, respectively. By setting up the magnetic field properly, a close current loop of drifting secondary electrons is formed. This electron trapping effect increases the collision rates between the electrons and sputtering gas molecules. The working pressure in the magnetron sputtering system is 10^{-5} to 10^{-3} Torr, and so the sputtered particles traverse the discharge space without collisions, consequently yielding high deposition rates. In the ion beam sputtering system, the incident ions are generated by an ion source separated from the sputtering chamber. The pressure in the sputtering chamber is typically 10^{-5} to 10^{-4} Torr range. Ion beam sputtering systems are used in sputter etching of semiconducting devices and have gained interest in thin film deposition.

1.3.3 Plasma immersion ion implantation and deposition

Plasma immersion ion implantation and deposition (PIII&D) is a versatile technique that can conduct simultaneous and sequential ion implantation and deposition, owing to a combination of the advantages offered by conventional plasma and ion beam technologies (Lu et al., 2012). The uniqueness of PIII&D over conventional ion

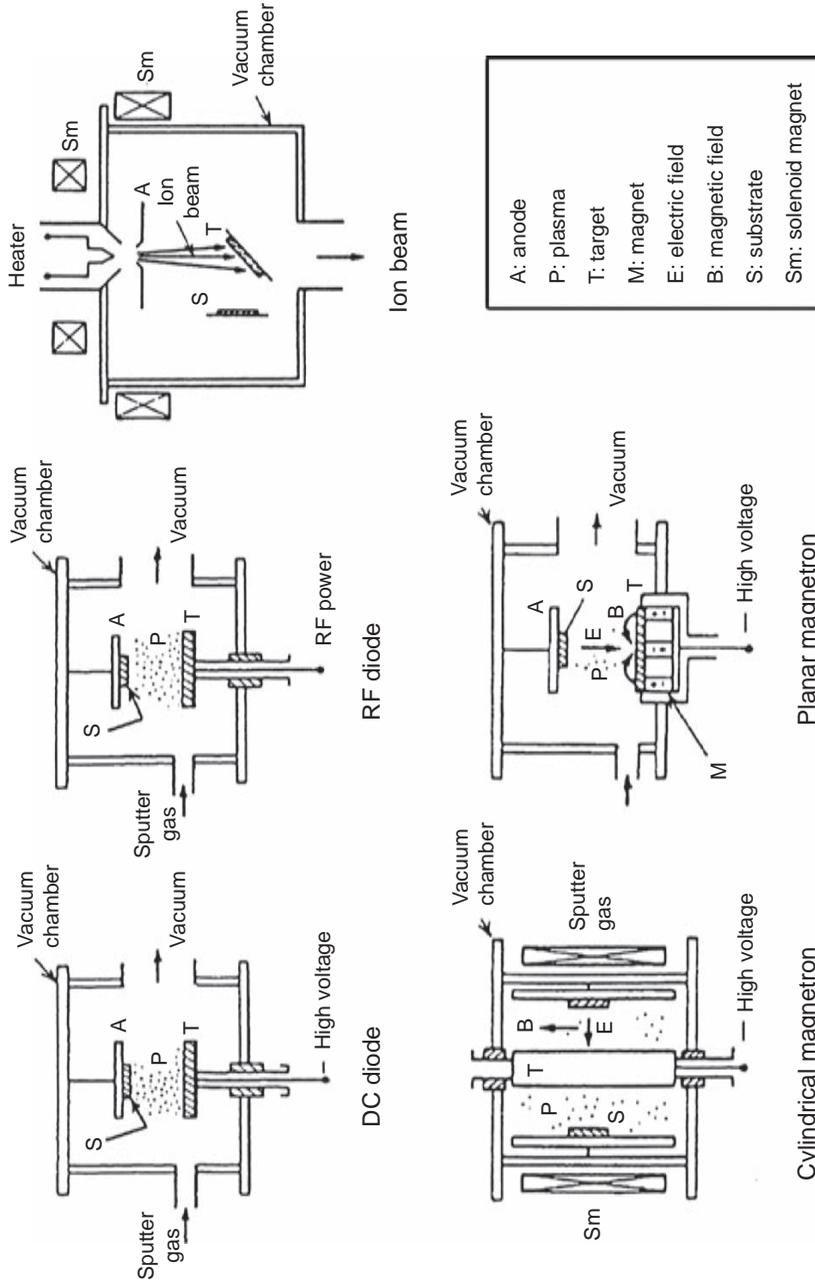


Figure 1.8 Sputtering deposition systems. Reprinted with permission from Wasa, K., 2012b. Sputtering systems. In: Wasa, K., Kanno, I., Kotera, H. (Eds.), Handbook of Sputtering Technology, second ed. William Andrew Publishing, Oxford, pp. 77–139; Adachi, H., Wasa, K., 2012. Thin films and nanomaterials. In: Wasa, K., Kanno, I., Kotera, H. (Eds.), Handbook of Sputtering Technology, second ed. William Andrew Publishing, Oxford, pp. 3–39.

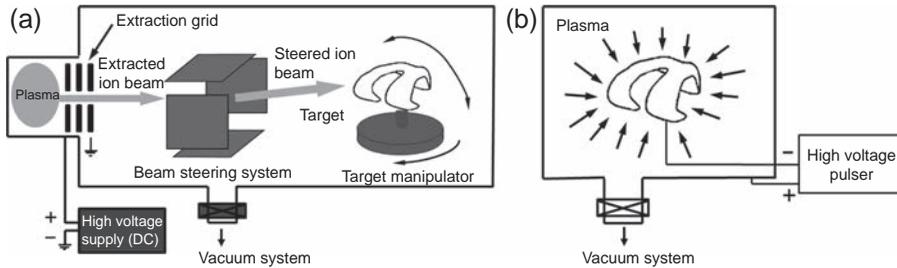


Figure 1.9 Schematic illustrations: (a) Conventional beam line ion implantation and (b) plasma immersion ion implantation.

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implantation stems from the separation of the ion source and target. Conventional ion implantation (Fig. 1.9(a)) is a line-of-sight process in which ions are extracted from plasma in an extraction system, accelerated as a beam to high energy, and then bombard the sample. Owing to the small cross-sectional area of the ion beam, either beam or sample rotating must be performed to achieve uniform implantation into a large sample. Ion implantation is suitable for planar substrates such as silicon wafers, but for complicated surfaces, sample rotation is required for uniform implantation, which adds complexity and limits the size of the samples (Liu et al., 2008).

In the PIII&D system, rather than using conventional ion extraction, the sample is immersed in plasma normally sustained by an external plasma source (Fig. 1.9(b)). The plasma can be generated by a number of plasma sources, including hot filament, RF, and electron cyclotron resonance. The negative high voltage applied to the sample accelerates electrons away from the sample surface while positive ions are accelerated from the plasma to bombard the sample surface. Under the sample bias, a plasma sheath through which ion implantation takes place forms around the sample (Anders, 2000). The plasma sheath, which dictates the implantation process, thus has an important role in PIII&D and can be used to predict the processing parameters and results, including the implantation current, implantation fluency, and depth profile. Because the sample is enshrouded by the plasma sheath, PIII&D can be used to process nonplanar ones. PIII&D has many advantages over conventional implantation; for example, high ion current density, relatively short processing time (eg, minutes), high dose rates (eg, $10^{14} \text{ cm}^{-2} \text{ s}^{-1}$), wide ion energy range ($10\text{--}10^5 \text{ eV}$), large implantation areas (hundreds square centimeters), and treatment of devices with complex shapes without special target manipulation (Pelletier and Anders, 2005; Chu et al., 1996).

Since its inception in the late 1980s, PIII&D has spurred many significant applications, particularly semiconductor and microelectronics processing (Chu et al., 1996; Anders, 2002; Chu, 2004). PIII&D has also gained great attention in biomedical engineering related to the surface modification of biomedical implants to enhance mechanical properties, bioactivity, biocompatibility, blood compatibility, and antibacterial activity (Huang et al., 2004; Chu, 2013). For example, magnesium alloys, which

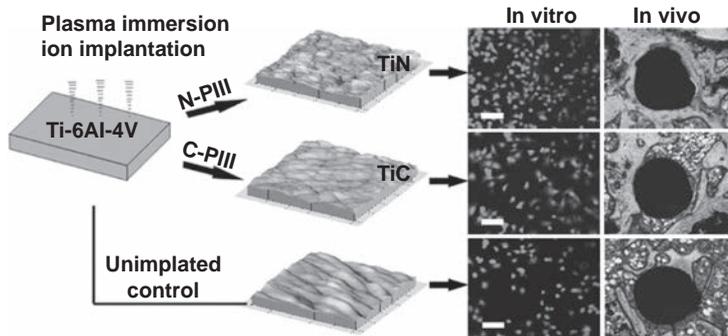


Figure 1.10 Schematic illustration of enhanced cell adhesion and early bone formation on Ti-6Al-4V after nitrogen and carbon plasma immersion ion implantation.

Reprinted with permission from Zhao, Y., Wong, S.M., Wong, H.M., Wu, S., Hu, T., Yeung, K.W.K., Chu, P.K., 2013. Effects of carbon and nitrogen plasma immersion ion implantation on *in vitro* and *in vivo* biocompatibility of titanium alloy. *ACS Appl. Mater. Interfaces* 5, 1510–1516.

possess unique properties such as natural biodegradability, experience fast corrosion in the physiological environment. The corrosion resistance of the magnesium alloys can be enhanced by PIII of gaseous or metallic elements such as oxygen (Wu et al., 2012a), chromium (Xu et al., 2012), aluminum (Wu et al., 2012b), zirconium (Zhao et al., 2014), and so on. PIII&D has also been carried out on titanium and titanium alloys to improve bioactivity and biocompatibility (Maitz et al., 2005; Xie et al., 2005; Zhao et al., 2013). Zhao et al. (2013) conducted nitrogen and carbon plasma immersion ion implantation on Ti-6Al-4V to form surface layers of TiN and TiC (Fig. 1.10). *In vitro* studies reveal improved cell adhesion and proliferation, and early bone formation is enhanced by *in vivo* tests. Moreover, there has been considerable research on the treatment of biomedical and degradable polymers such as poly(butylene succinate) (Wang et al., 2009) and polytetrafluoroethylene (Wang et al., 2010, 2012) by PIII&D to enhance surface bioactivity and biocompatibility.

1.4 Electrophoretic deposition

Thin film deposition methods based on gas-phase processes such as CVD, evaporation, and sputtering are straightforward and thin films with good purity and structural properties can be produced. However, there are some drawbacks, such as the strict instrumentation requirement, relatively high processing cost, as well as gaseous waste treatment. In comparison, chemical and electrochemical solution methods are cost-effective and waste is confined to the solution.

Electrophoretic deposition (EPD) is a wet electrolytic deposition technology for thin films. EPD employs the electrophoresis mechanism, as illustrated schematically in Fig. 1.11. The electric field is applied between two electrodes and charged particles dispersed or suspended in a liquid medium move toward the oppositely charged

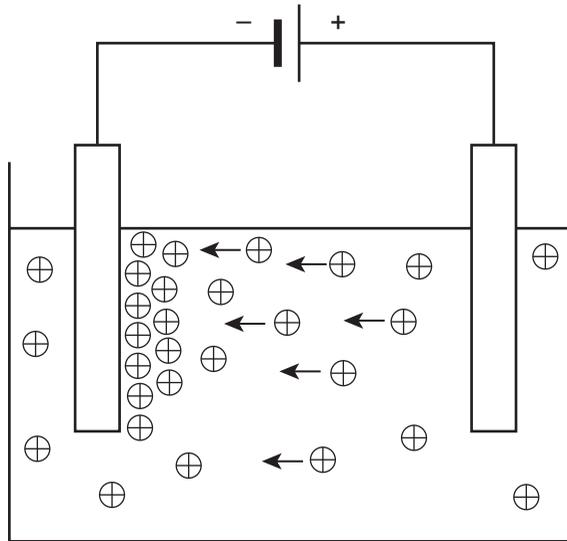


Figure 1.11 Two-electrode cell for electrophoretic deposition showing positively charged particles in the suspension migrating toward the negative electrode. Reprinted with permission from Corni, I., Ryan, M.P., Boccaccini, A.R., 2008. Electrophoretic deposition: from traditional ceramics to nanotechnology. *J. Eur. Ceram. Soc.* 28, 1353–1367.

electrode (electrophoresis), followed by accumulation of particles on the deposition electrode in an ordered manner, producing a relatively compact and homogeneous film (deposition) (Corni et al., 2008). Stability of the suspension is critical to EPD to allow free movement of the charged particles in the solution. The charged particles can be fine powders, colloids, or macromolecules, and EPD is a versatile method to fabricate films composed of ceramics, metals, polymers, and even organic/inorganic hybrid materials.

On the heels of major development of EPD in the deposition of bulk materials and coatings, the application of EPD to biomaterials starts with the preparation of hydroxyapatite (HA) $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ coatings on Ti (Boccaccini et al., 2010; Ducheyne et al., 1986). In a typical process involving the EPD of HA coatings, HA powders are homogeneously dispersed in ethanol to obtain a colloidal suspension and electrophoretically deposited on stainless steel. Results show that a long deposition time (more than 90 s) results in spalling owing to shrinkage from drying, but a repetitive deposition method instead of single deposition can be employed to overcome the spalling problem (Wang et al., 2002). EPD has also found success in the production of other bioceramic coatings or metallic films. Zhang et al. (2010) prepared TiO_2 films on nickel with low-temperature EPD. The photocatalytic activity of the TiO_2 film is evaluated by monitoring the degradation rate of methyl orange (MO), and the degradation rate of MO increases with the amount of TiO_2 . Zhu et al. (2012) reported an EPD method for the fabrication of gold nanoparticle thin films on indium tin oxide as sensitive SERS substrates.

Biomedical applications of EPD have been extended to the deposition of functional composite coatings and multilayer films (Fig. 1.12). Jiang et al. (2010) prepared pure chitosan and CS/G coatings on titanium substrates via EPD. The coatings possess a similar macroporous structure and the shear bonding strength of the CS/G coatings increases with the gelatin contents. In vitro biological tests demonstrate that human MG63 osteoblast-like cells have better affinity on the coatings with larger gelatin contents. Pang et al. (2009) prepared hydroxyapatite (HA)–CaSiO₃(CS)–chitosan coatings by cathodic EPD. The EPD HA–CS–chitosan composite coatings have monolayered or laminated structures containing different layers, as shown in Fig. 1.12(a). Potentiodynamic polarization studies coupled with electrochemical impedance spectroscopy indicate that the composite coatings enhance the corrosion protection of the stainless-steel substrate. EPD has also been used to codeposit other

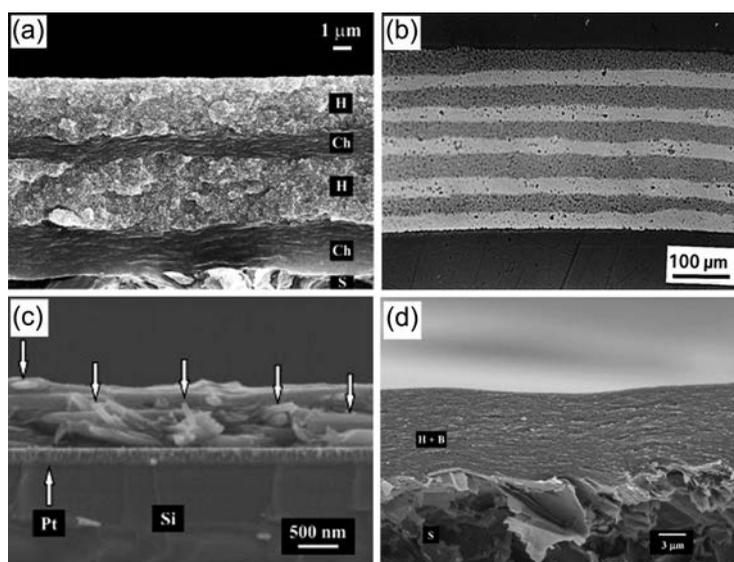


Figure 1.12 Cross-sectional scanning electron microscopy images of EPD-fabricated composites or multilayered coatings: (a) Laminate coatings of chitosan (Ch) and HA (H) with different layers on a graphite substrate (S); (b) 10 alternating layers of Al₂O₃ and ZrO₂; (c) polyacrylic acid films containing halloysite nanotubes (white arrows) on the platinumized silicon wafer substrate; (d) sodium hyaluronate and bovine serum albumin composite films (H + B) on a graphite substrate (S).

Reprinted with permission from Pang, X., Casagrande, T., Zhitomirsky, I., 2009. EPD of hydroxyapatite–CaSiO₃–chitosan composite coatings. *J. Colloid Interface Sci.* 330, 323–329; Ferrari, B., Sánchez-Herencia, A.J., Moreno, R., 1998. Aqueous EPD of Al₂O₃/ZrO₂ layered ceramics. *Mater. Lett.* 35, 370–374; Wang, Y., Deen, I., Zhitomirsky, I., 2011. EPD of polyacrylic acid and composite films containing nanotubes and oxide particles. *J. Colloid Interface Sci.* 362, 367–374; Ma, R., Epanand, R.F., Zhitomirsky, I., 2010. Electrodeposition of hyaluronic acid and hyaluronic acid-bovine serum albumin films from aqueous solutions. *Colloids Surf. B Biointerfaces* 77, 279–285, respectively.

materials and realize further functionalization of composite coatings such as Al_2O_3 – ZrO_2 -layered ceramics (Ferrari et al., 1998), polyacrylic acid films containing nanotubes and oxide particles (Wang et al., 2011), and hyaluronic acid–bovine serum albumin films (Ma et al., 2010).

1.5 Sol-gel method

The sol-gel technique has emerged as a versatile method for the preparation of oxide thin films and oxide-containing composite films. The sol-gel process consists of three parts: preparation of the precursor solution, deposition of the sol onto the substrate, and heat treatment for densification. The precursors are commonly metal alkoxides in organic solvents or metal salts in aqueous solutions, depending on the nature of the molecular precursors (Livage and Ganguli, 2001). Sol deposition is normally performed by means of spin- or dip-coating techniques, and the thickness of the thin film can be controlled at the submicrometer level by varying the withdrawal or spinning rate in the case of dip and spin coatings (Brinker et al., 1992). The abundance of choice in each step endows the sol-gel method with versatility and renders the controllability of thin film structural properties. In a review of sol-gel deposition of zinc oxide thin films, Znaidi (2010) summarized the chemical and physical parameters influencing the structural properties of thin films in the sol-gel process.

In addition to better control of the chemical composition and microstructure of the films, the sol-gel method offers advantages over other thin film processes including the preparation of homogeneous films, reduced densification temperature, simpler equipment, and lower cost (Liu et al., 2010). There has been extensive research on the use of sol-gel deposition to improve the bioactivity, blood compatibility, and antibacterial properties of biomaterials. Table 1.1 lists common thin films fabricated by the sol-gel method, including the chemical systems used and biomedical applications.

1.6 Spraying processes

Thermal spraying refers to the spraying of molten or semimolten particles onto a substrate at a high speed to prepare coatings (0.5–2 mm thick). According to the different heating sources to melt the particles, thermal spraying can be divided into flame, electrical arc, plasma, and detonation-gun spraying (Pawłowski, 2008). Plasma spraying is the most common method, typically composed of atmospheric plasma spraying and vacuum plasma spraying. In plasma spraying, illustrated in Fig. 1.13(a), the high energy of the high-frequency electrical arc ignited between the anode and cathode with the aid of the plasma-forming gas (Ar, He, H_2 , N_2 , or mixtures) melts and sprays the particles onto a substrate at a high velocity. The melted or partially melted particles undergo splat formation, splat layering, and coating formation before they flatten and solidify on the substrate (Fauchais, 2004). Currently, DC plasma arc devices dominate the commercial market, whereas RF or inductively coupled plasma devices have a few commercial applications in plasma spraying (Liu et al., 2004).

Table 1.1 Thin films fabricated by the sol-gel process and their biomedical applications

Films	Substrate	Coating technique	Pre-heat treatment (°C)	Post-heat treatment (°C)	Application	References
Carbon nanotube/hydroxyapatite	Ti-6Al-4V	Dip coating	50	500	Biocompatibility	Abrishamchian et al. (2013)
TEOS-MTES-SiO ₂	Stainless steel	Dip coating	r.t.	450	Bioactivity	Ballarre et al. (2010)
TiO ₂ , Nb ₂ O ₅ , SiO ₂ , SiO ₂ -TiO ₂	Pure titanium	Spin coating	150	450	Osteoblast responses	Ochsenbein et al. (2008)
Ag-TiO ₂	Silicon	Spin coating	100	500	Antibacterial	Yu et al. (2011)
Ag-SiO ₂	Glass	Dip coating	100	200-600	Antibacterial	Jeon et al. (2003)
Silica	Ti-6Al-4V	Dip coating	-	r.t.	Controlled release of vancomycin	Radin and Ducheyne (2007)
TiO ₂ /SrFe ₁₂ O ₁₉ composite	316L stainless steel, NiTi alloy	Spin coating	-	500	Blood compatibility	Liu et al. (2011)

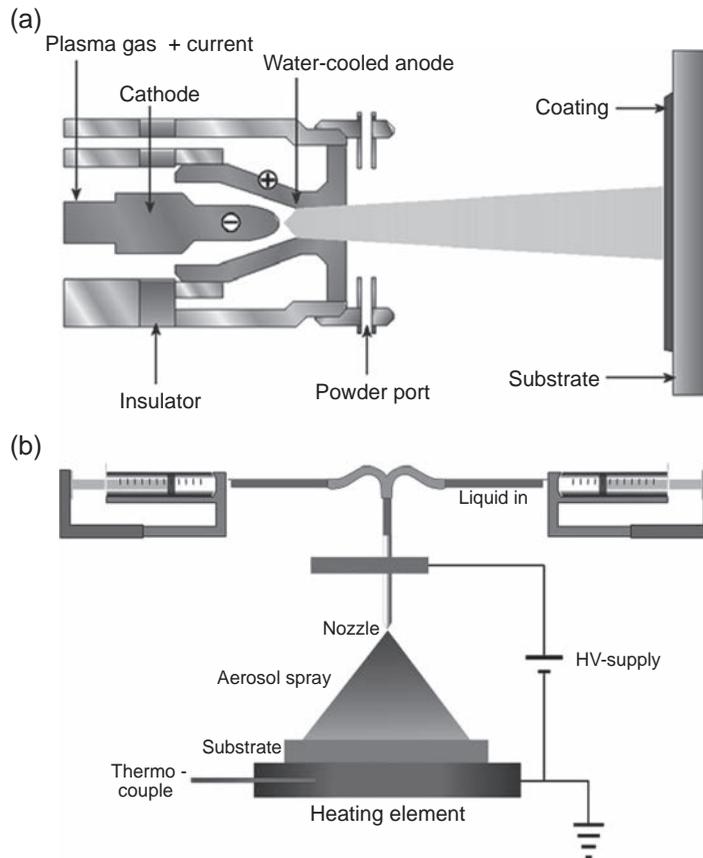


Figure 1.13 (a) Schematic diagram of the plasma spray process and (b) experimental setup of the electrostatic spray deposition technique.

Reprinted with permission from Vencel, A., Mrdak, M., Cvijovic, I., 2006. Microstructures and tribological properties of ferrous coatings deposited by APS (Atmospheric Plasma Spraying) on Al-alloy substrate. *FME Trans.* 34, 151–157; Leeuwenburgh, S., Wolke, J., Schoonman, J., Jansen, J., 2005. Influence of deposition parameters on chemical properties of calcium phosphate coatings prepared by using electrostatic spray deposition. *J. Biomed. Mater. Res. A* 74, 275–284.

As a surface modification technique for biomaterials, plasma spraying is a favorable method to deposit bioceramic coatings. Hydroxyapatite coatings provide orthopedic implants with a mineral phase similar to natural hard tissues and improve bioactivity and osteoconductivity. Considerable research efforts have been devoted to producing plasma-sprayed HA coatings on metallic implants and resulting applications to dentistry and orthopedics (Sun et al., 2001). In addition, other coatings such as CaSiO_3 and TiO_2 have been plasma sprayed and confirmed to reinforce apatite formation on the surface (Chen et al., 2008; Liu et al., 2001, 2005).

Electrostatic spray deposition (ESD) has been developed to prepare bioactive calcium phosphate coatings. The basic principle of ESD encompasses the

generation and spraying of an aerosol and dispersion of charged particles or droplets by means of electrostatic atomization of the inorganic or organometallic precursors (Leeuwenburgh et al., 2003). As shown in Fig. 1.13(b), high voltage between the nozzle and grounded substrate (typically between 6 and 15 kV) produces droplets at the tip of the nozzle, forming a spray of highly charged droplets. These spray droplets impinge onto the heated substrate as a result of the applied potential and lose their charge. Consequently, a thin inorganic layer is formed by complete solvent evaporation (Leeuwenburgh et al., 2005).

1.7 Conclusion

In summary, common thin film deposition technologies for surface modification and the engineering of biomaterials have been reviewed with an emphasis on the fundamentals and technology of each method. Examples of fabricated films and their applications in the biomedical fields are described. Properties such as film thickness, mechanical properties, and surface chemistry produced by different techniques can differ greatly and the choice requires systematic study and comparison. From the perspective of the development of thin film deposition techniques, the combination of the different techniques, chemical and physical, can realistically enable the exploration and expansion of existing techniques for the fabrication of future films and coatings.

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