## Nanocoatings and Ultra-thin Films: Technologies and Applications

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*Nanocoatings and ultra-thin films: Technologies and applications* is both a reference book and a tutorial for understanding the most common thin-films and coating techniques. The book encompasses recent approaches and future trends in coating and thin films technology, looking at essential innovations in the development of industrial nanocoatings and ultra-thin films based on new findings resulting from basic and applied research in the fields of both physics and chemistry.

Ultra-thin films and nanocoatings play a major role in many areas such as micro- and nanoelectronics, machine building, car and aircraft manufacturing, robotics, etc. Nanocoatings, in particular, represent the interface between the product and the environment and therefore determine not only aesthetic aspects of goods, but also important specific properties such as, for example, anti-corrosion, self-cleaning, chemical and scratch resistance, etc. The term 'nanocoatings' is usually used when the coating is nanostructured or its thickness is in the nanometer scale. Nanostructuring is usually applied because of its ability to increase hydrophobicity, radiation hardness, and corrosion resistance and because it makes materials much more flexible.

The goal of this book is to discuss the basics of ultra-thin films and nanocoatings technologies and their synthesis techniques, surface characterization, and performance for possible industrial applications. It addresses important questions frequently posed by end-users such as design engineers, coaters, and coatings suppliers in their quest for multifunctional and superior coating qualities for industrial applications. The contributions in this book emphasize thin films, self-healing coatings, self-cleaning coatings, super-hard nanocoatings, corrosion, tribological, nano-ceramic and nanocomposite coatings with respect to their mechanical and physical properties.

Chapter 1 addresses the most common coating techniques. It includes recent developments and future trends in coatings technology and considers the essential innovations in the development of industrial coatings. The chapter highlights future improvements in coating processes based mainly on: reduction of the number of coating layers; full automation of the coating process; controlling the end product colour through a module method and automatic quality control.

Chapter 2 discusses the nanostructuring of thin films of amphiphilic macromolecules and nanomaterials at the air–water interface. The chapter introduces several synthesized amphiphilic materials which have been recently used in the Langmuir–Blodgett (LB) technique. The surface chemistry and properties of the synthesized amphiphilic materials at the air – water interface are also described. Examples of thin films applications using the LB technique are discussed.

Chapter 3 provides a comprehensive analysis of vacuum deposition methods for nanocoating and the production of functional graded (FG) multilayers. A general approach of the FG layer-by-layer synthesis is based on a paradigm of the type of connectivity of the internal structure. The objective of the chapter is to demonstrate the particularities and versatility of PVD, CVD, laser-, electron-, and ion-assisted technologies in the engineering of the FG nanocoatings with control microstructure. The chapter also provides a description of the nanoperspectives of FG thin films and surface structures with nanoelectromechanical systems (NEMS) properties.

Chapter 4 discusses surface-initiated polymerization for nanocoatings. In this chapter, thin polymer layer– surface conjugates are proposed as appropriate materials for studying surface/interface physicochemical properties and material interactions with the environment, allowing performance control over the entire system. Recent advances in surface-attached polymer layers are presented, and thermodynamic and kinetic aspects of polymer physi- and chemisorption are discussed. The chapter also summarizes the preparation methods for polymergrafted surfaces with the emphasis on controlled processes able to achieve polymer surfaces meeting well-defined criteria. A comparison between the unique properties of polymer brushes and the bulk characteristics or the physisorbed layers is highlighted.

Chapter 5 reports the most common and advanced methods for characterization and surface-sensitive analysis of nanocoatings and ultra-thin films. A correlation between the linear potential sweep and impedance measurements for copper specimens under different tarnishing treatments is discussed. The changes in the dielectric constant caused by water absorption and the pigment/polymer proportions and porosity of the organic coatings are described with a reasonably good approximation using electrochemical methods. These coatings are characterized by different analytical techniques such as AFM, XPS, infrared, Raman and Mössbauer spectroscopies, XRD, ion spectroscopy, glow discharge optical emission spectroscopy, electronic microscopy, scanning acoustic microscopy, and the Kelvin probe force microscopy.

Chapter 6 provides an overview of conventional and advanced coatings for industrial applications and describes the role of coating technologies in some important industrial applications. The chapter also presents a critical review of recent research-and-development work on advanced coatings such as smart coatings, 'super'hard coatings, multifunctional coatings, .etc. The most important aspects of coating technologies for the automotive industry and for sensing, packaging, and biocompatible applications are discussed.

Chapter 7 provides a general overview of the main types of nanocoatings for architectural window glass. Glass plays an important role in building design because of its influence on thermal and visual comfort in buildings. Highly transparent coatings are deposited onto architectural windows to be employed in commercial and residential buildings for the purpose of saving energy for heating and air conditioning. They offer environmental benefits because they reduce heat loss and allow passive solar heat gain, reducing the energy consumption required to heat a building as well as energy related  $CO_2$  emissions from buildings.

Chapter 8 discusses the challenges of nanocoatings and ultra-thin films for packaging applications. Packaging technology is of strategic importance as it can be a key to competitive advantage in modern industry. An innovative pack design can open up new distribution channels, providing a better quality of presentation, enabling lower costs, increasing margins, enhancing brand differentiation, product safety and integrity, and improving the logistics service. Thus, there is a persistent challenge to provide cost-effective pack performance, with health and safety being of paramount importance. At the same time, there is a continuous legislation and political pressure to reduce the amount of packaging used and packaging waste. The chapter reports a variety of polymers currently used in packaging and the most widely used plastics in flexible packaging. It also reports different designs and processing techniques used to produce packaging products.

Chapter 9 deals with conventional coating technologies and smart nanocoatings for corrosion protection in aerospace engineering. The types and factors which influence corrosion are reviewed as well as the protective coatings that have been in use or which have shown potential for future applications. In addition, particular attention is given to functional nanocoatings for sensing corrosion, nanostructured coatings which self-heal when either corrosion starts or the corrosivity of the environment becomes critical, and other coating properties important in reducing maintenance costs. The chapter concludes that fundamental and applied research in the area of sensorbased, corrosion active and anti-icing/self-cleaning smart coatings is expected to grow in the near future, contributing to the generation of high performance, added-value products.

Chapter 10 discusses nanoimprint lithographic (NIL) techniques for electronics applications. The potential of these techniques to surpass photolithography in resolution, and, at the same time, to allow mass fabrication at a lower cost is highlighted. Current and potential uses of NIL are discussed in such fields as data storage, optical components, image sensors, and phase change random access memory devices. Challenges faced by nanoimprint lithography in becoming a standard fabrication technique are also considered.

Chapter 11 addresses some technological approaches for the fabrication of ultra-thin membranes for sensor applications and flexible, stretchable, foldable electronics. The discussion focuses on graphene and two dimensional sheets of layered compounds. The potential to build multifunctional 3D nanoarchitectures based on 2D graphene hybridized with 1D semiconductor nanostructures is highlighted. The chapter also reviews the fabrication of ultra-thin GaN membranes of nanometer scale thickness by using the concept of surface charge lithography based on low energy ion treatment of the sample surface with subsequent photoelectrochemical etching.

Chapter 12 discusses the use of nanostructured coatings as tribological surfaces for both friction and wear reduction with examples from state-of-the-art research. The chapter gives a general overview of common friction and wear mechanisms encountered in engineering applications. Moreover, it provides a brief review of methods used to deposit nanostructured coatings on substrates. Different advanced techniques for friction and wear characterization of nanostructured coatings and the scale dependence of tribological properties are discussed. The challenges encountered in extrapolating laboratory experiments to field applications are discussed.

Chapter 13 looks at the concept of smart materials/coatings – terms usually applied to materials able to change their properties in response to an external stimulus such as light or temperature. New insight is provided into self-cleaning smart coatings and the chapter expands to cover the major features of the photocatalytic materials developed to date. The chapter also gives a historical overview of TiO<sub>2</sub> photocatalysis in order to clarify the fundamental characteristics of the photocatalysis processes that take place on TiO<sub>2</sub> surfaces. The electronic processes are also discussed, highlighting the main factors controlling the intensity of light absorption by the molecule or substrate. The chapter discusses actual and potential applications of TiO<sub>2</sub> photocatalysis in industry and in the development of self-cleaning glass materials, giving some practical examples of the application of TiO<sub>2</sub> nanoparticles in environment protection.

The book is targeted for researchers working in the fields related to nanotechnologies, materials science, nanocoatings and ultra-thin thin films. It is also recommended for students and PhD students from the fields involved.

The book was presented to the scientific community of the Republic of Moldova by Mircea Bologa, Ion Bostan and Teodor Shishianu, members of the Academy of Sciences of Moldova, at the Academy of Sciences of Moldova, on November 25, 2011.