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Chapter 9

Silver Nanoparticles Fabricated Using Chemical Vapor Deposition and Atomic Layer Deposition Techniques: Properties, Applications and Perspectives: Review

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Abstract

Silver nanoparticles with unique physicochemical properties and high biocide activity attract great interest in the design and in the manufacture of the new generation materials intended for biomedical technologies. This review aims to provide assessment of the bioactivity and usefulness of Ag-based materials in biomedical technologies, which are produced with the use of chemical vapor deposition (CVD) and atomic layer deposition (ALD) methods. The use of CVD and ALD technologies in the fabrication of silver layers, nanoparticles, and nanocomposites are discussed in the first part of this chapter. The second half of this review deals with the topics associated with the release of silver ions from nanoparticles or nanolayers and discusses the antimicrobial activity, bio-integration properties and toxicity of these materials.

Keywords: silver, silver-based materials, CVD, ALD, bioactivity, biomedical materials

1. Introduction

The rapid development of nanotechnologies is a result of the numerous applications of nanomaterials in various fields of our life. The metallic nanograins or metallic nanolayers, of either simple or composite nature, are important materials in the improvement of such traditional areas as electronics, optics, and catalysis. However, in last few years we have observed a great interest in the application of these nanomaterials in biological, biomedical, pharmaceutical, cosmetic, food, and textile technologies [1–5]. The use of different methods offers the possibility of the fabrication of nano-sized materials (materials in which at least one dimension is less than 100 nm) of different structure, surface morphology,

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physicochemical properties, and bioactivity [6–9]. From the medical point of view, it is interesting that silver as an antimicrobial agent has accompanied human civilization since ancient times. The use of silver vessels or putting a silver coin/spoon into tanks in order to preserve drinking water from spoilage by bacteria and algae, was practiced by ancient Egyptians and Greeks, as well as by sailors in times of great geographic discoveries [10]. In modern times, silver (usually used as colloidal silver) is applied to treatment water and its disinfection. The system working on the board of International Space Station is a good example [9, 11]. Moreover, the fabrication of this metal coating on the surface of medical devices or pieces of furniture, and also incorporation of Ag nanoparticles to the building and textile materials, influences the reduction of the hospital-related infections [12–14]. Silver nanoparticles (AgNPs) are also component of many health and cosmetic products due to their antimicrobial activity and deodorizing properties [15, 16]. Based on previous results, it is noted that the above-mentioned nanoparticles exhibit antimicrobial activity against 650 strains of pathogenic microorganisms such as bacteria, fungi, viruses, molds, and yeasts [17, 18]. A number of mechanisms have been proposed to explain the antimicrobial activity of AgNPs: (1) blocking the active respiratory chains of organisms; (2) disrupting the cellular membrane leading to leakage of cellular contents; (3) binding to the functional groups of microbial proteins that lead to protein denaturation and DNA malfunctions; and (4) blocking of nutrient transportation enzymes across the cell membrane [18]. The above-mentioned biological properties of the Ag nanoparticles and nanolayers depend strongly on their structure, shape, size, surface morphology, and the substrate used in the synthesis.

Silver may form continuous nanolayers and/or dispersed nanoparticles on the substrate surface or it can be incorporated within the matrix (ceramic, glass, and polymer). Generally, two strategies based on wet chemistry and vapor phase deposition are used for the preparation of Ag-containing nanomaterials. Analysis of the literature reports showed that the reduction processes of $AgNO_3$ are the main methods, which are used in the fabrication of AgNPs both on the substrate surface as well as in the form of the dispersed particles in colloidal systems, glasses, or polymers [12, 15]. According to these reports, the wet chemical techniques are mainly used for the fabrication of silver nanoparticles [9]. In these methods, the colloidal silver is obtained by the use of three components: (a) silver precursor, predominantly $AgNO_3$; (b) reducing agent – for example, $NaBH_4$, citric acid or its sodium salt, gallic acid, ascorbic acid [9, 19–22]; and (c) stabilizing agents—for example, polyvinyl alcohol, polyvinyl pyrrolidone, polyethylene glycol, ethylene diamine tetra-acetic acid [23, 24]. The nucleation of nanoparticles and their growth in defined conditions (temperature, pH, reduction agents, and stabilizing agents) leads to the formation of similar size and shape particles [9, 23]. Dried Ag nanopowders, which can be added to, for example, polymeric, glass, or ceramic matrix, were obtained by freeze-drying of the colloidal solution [20]. Biosynthesis of AgNPs is a promising technique which has been intensively studied recently [25–27]. It involves the reduction of silver salt (e.g. silver nitrate) by such reducing agents as plants, bacteria, and fungi [27, 28]. The great interest of the above-mentioned method is due to its potential use in medicine (especially in cancer therapy and diagnostic)

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as the procedure allowing for obtaining nontoxic antimicrobial agent [26, 28]. The need to the fabrication of silver coatings, both continuous as well as composed of dispersed metallic grains on the surface of metallic, ceramic, or polymeric substrates, requires the use of other methods. Often used photochemical synthesis of AgNPs on the surface of titania nanotube (TNT) coatings is a good example [29–31]. In this method, TNT substrate is soaked in $AgNO_3$ solutions of different concentration, and after cleaning with deionized water and drying, is irradiated using UV light at room temperature. Silver particles with diameters 10–70 nm were deposited on the top edges and walls of ca. 50–180 nm TiO_2 tubes [30, 31]. AgNPs on the surface of different titania substrates may be also prepared using electrodeposition and electrochemical methods [32–34]. Above-mentioned techniques enabled the deposition of dispersed Ag particles of diameters ca. 2–12 nm on the surface of titania particles or nanotubes.

Chemical vapor deposition (CVD) and atomic layer deposition (ALD) belong to the strategy based on the fabrication of materials from vapor phase. Analysis of literature reports revealed that both methods are not widely used in the production of biomaterials, although both methods allow exact control of the nucleation and growth of metallic single grains or layers. It may be associated with necessity for the use of vacuum and high temperatures as in the case of CVD processes, which in turn translates into high price of the final product. However, the rapid development of both above-mentioned methods, related to the introduction of new precursors, improvement of the equipment, and optimization of the deposition conditions, has led to increased interest of their application in the production of materials, with strictly defined structure, morphology, physicochemical and biological properties, and also characterized by high purity. Therefore, in this chapter we have focused on a more detailed discussion on the use of CVD and ALD methods for the production of silver-based materials, their properties and biological activity.

2. Chemical vapor deposition

Chemical vapor deposition (CVD) is a technique which allows the synthesis of nanometric layers of inorganic materials on the surface of 3D substrates. The deposition process occurs in three successive stages: (i) introduction of the volatile precursor by carrier gas to the reactor chamber; (ii) adsorption of precursor vapors on the substrate surface and the formation of intermediate products; and (iii) decomposition of these products on the heated substrate followed by nucleation and growth of the solid layer/grains, and the formation of volatile by-products and their removal from the chamber by the carrier gas [35]. Among the main factors that influence the deposition process and the quality of produced nanomaterials, the following ones can be highlighted: the precursor delivery method, total pressure in the reactor chamber (p), carrier gas and its chemical properties, substrate temperature (T_D), substrate properties, flow rate of precursor vapors, deposition time (t), and deposition rate. Among these factors, precursors as a source of formed material, seem to be the most important factor. The CVD precursor

should be characterized by: (a) the appropriate volatility to achieve the highest possible concentration of the precursor in vapors; (b) the thermal stability of the compound which avoids its premature degradation during the transportation of vapors by carrier gas; (c) its ability for thermal decomposition on the substrate surface leading to the deposition of desirable materials; (d) inexpensive and simple synthesis; and (e) low toxicity. Considering these reports, we find that for CVD, two types of compounds are usually used as silver precursors, namely inorganic silver salts and volatile silver (I) complexes. Silver nitrate ($AgNO_3$) is the widely used precursor in such techniques as the flame-assisted CVD (FACVD) and the atmospheric pressure CVD (APCVD) [36–38]. The first of these method enables the deposition of metallic silver layers of thickness 60–90 nm [36] or 60–250 nm [37] on the substrate surface heated to the temperature T_D = 573 K at atmospheric pressure. The advantage of this method is the ability to the formation of Ag-metal oxide nanocomposite coatings (e.g. TiO_2 [36], SiO_2 [39]) in one deposition process on large substrate areas. The nanocomposite coatings on the textile surface, composed of silicon dioxide with in situ incorporated Ag nanoparticles were produced by APCVD technique [38]. In the classical CVD techniques (metal-organic CVD (MOCVD), aerosol-assistant CVD (AACVD), plasma-enhanced CVD (PECVD)), a variety of volatile silver(I) compounds are used as precursors [35, 40]. This group includes the silver(I) compounds with β-diketonates and carboxylates (mainly perfluorinated carboxylates), as well as their complexes [Ag(A)(L)] (A = carboxylate or β-diketonate groups, L = trimethyl phosphine (PMe_3), trimethyl phosphine (PEt_3), vinyltriethylsilane (VTES), bis(trimethylsilyl)acetylene (BTMSA), bis(trimethylsilyl)ethyne (BTMSE)) [35, 40, 41]. The detailed data concerning silver(I) complexes, which are mainly used as CVD precursors are listed in **Table 1**. Liquid Ag(I) β-diketonates and their complexes are precursors usually used in the fabrication of metallic nanofilms of appropriate electrical conductivity [35]. Results from our investigations showed that silver(I) carboxylates (solids) and their complexes with tertiary phosphines (oils) are the group of precursors, which may be applied to the deposition of coatings composed of dispersed metallic nanoparticles. Because of the weak volatility of Ag(I) acetate and Ag(I) tri-fluoro-acetate, these compounds cannot be used in conventional CVD methods, although pure silver continuous films were deposited from these compounds using laser-inducted CVD (LICVD) technique [35, 42]. The low volatile Ag(I) carboxylates and their complexes with tri-phenyl-phosphines were also introduced into the CVD reactor chamber as a solution or a suspension in AACVD method [43]. This enabled the deposition of metallic silver layers at temperatures below 573 K, but resulting materials were contaminated with carbon, oxygen, and phosphorus.

Considering results of these investigations, it is noted that silver(I) penta-fluoro-propionate ($Ag(OOCC_2F_5)$) exhibits particularly good properties as Ag CVD precursor [44, 45] since layers consisting of dispersed AgNPs of diameters d_{Ag} = 20–60 nm were obtained after 5 min of CVD process at 563 K on the surface of Si(111) substrate. After 10 min, particles already began to coalescence and after 30 min, the continuous metallic films, of thickness ca. 2.50 μm, were formed [44]. Under the same conditions, with titanium or Ti6Al4V alloy substrates, the layer composed of dispersed Ag grains of d_{Ag} = 35–40 nm were deposited (**Figure 1**). Using titania

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Precursor	Deposition temperature T_D (K)	Reactor pressure (hPa)	Carrier gas
[Ag(acac)]	473–523	—	H_2
[Ag(fod)(PMe_3)]	503–573	0.13	H_2
[Ag(fod)(PEt_3)]	503–533	0.13	H_2
[Ag(hfac)(PMe_3)]	523–723	0.07	—
[Ag(hfac)(PEt_3)]	523–623	0.07	—
[Ag(hfac)(VTES)]	433–553	0.13	—
[Ag(hfac)(BTMSA)]	423–523	0.13–13.0	—
[Ag(hfac)(BTMSE)]	373–473	13.0	—
$[Ag(tfpz)]_3$	523–623	0.67	Ar, H_2
[Ag($OOCCF_3$)]	873	No data	—
[Ag($OOCC_2F_5$)]	543–563	4	Ar
[Ag($OOCC_2F_5$)(PMe_3)]	483–563	4	Ar
[Ag($OOCC_2F_5$)(PEt_3)]	463–513	4	Ar
[Ag($OOCCF_3$)(P^nBu_3)$_2$]	573–623	1–50	N_2
[Ag($OOCC_2F_5$)(P^nBu_3)]	573–623	1–50	N_2
[Ag(OOC^tBu)(PMe_3)]	583	2–3	N_2
[Ag(OOC^tBu)(PEt_3)]	453–493	1.5–3	Ar, N_2
[Ag($OOCCH_2{}^tBu$)(PEt_3)$_2$]	453–553	2	Ar, N_2
[Ag($OOCCMe_2Et$)(PEt_3)$_2$]	473–553	2	Ar, N_2

acac:acetylacetonato;fod:2,2-dimethyl-6,67,78,8,8-heptafluoro-3,5-octanedionato;hfac:1,1,1,5,5,5-hexafluoroacetylacetonato; tfpz: trifluoroacetylacetonate; VTES: vinyltriethylsilane; BTMSA: bis(trimethylsilyl)acetylene; BTMSE: bis(trimethylsilyl) ethyne.

Table 1. The selected CVD metal-organic precursors used in the deposition of silver-based nanomaterials (the presented data are based on Ref. [35, 40–49]).

nanotube (TNT) coatings as a substrate, our studies show clear correlations between the tube diameters and the grain size, their dispersion and the position on the substrate surface (**Figure 1**). The silver particles of d_{Ag} = 35–45 nm were deposited on the surface of layers composed of dense packed tubes of diameter d_{TNT} = 20–30 nm. The increase of tube diameter to 30–60 nm caused metallic grains to be mostly located in their insides and thus it determines the direction of their growth. The rapid decrease of Ag grains diameter below 15 nm and their location on the tubes top edges and walls surfaces was observed for TNT coatings composed of separated tubes of d_{TNT} = 80–150 nm (**Figure 1**) [46]. The use of complexes [Ag(OOCR')(L)] (R' = C_2F_5, ^nBu, ^tBu, $CH_2{}^tBu$, CMe_2Et, L = PMe_3, PEt_3) revealed that the type of carboxylate group decided the morphology of deposited metallic layers as well as the way of the grain packing on the substrate surface (**Figure 2**) [47–49].

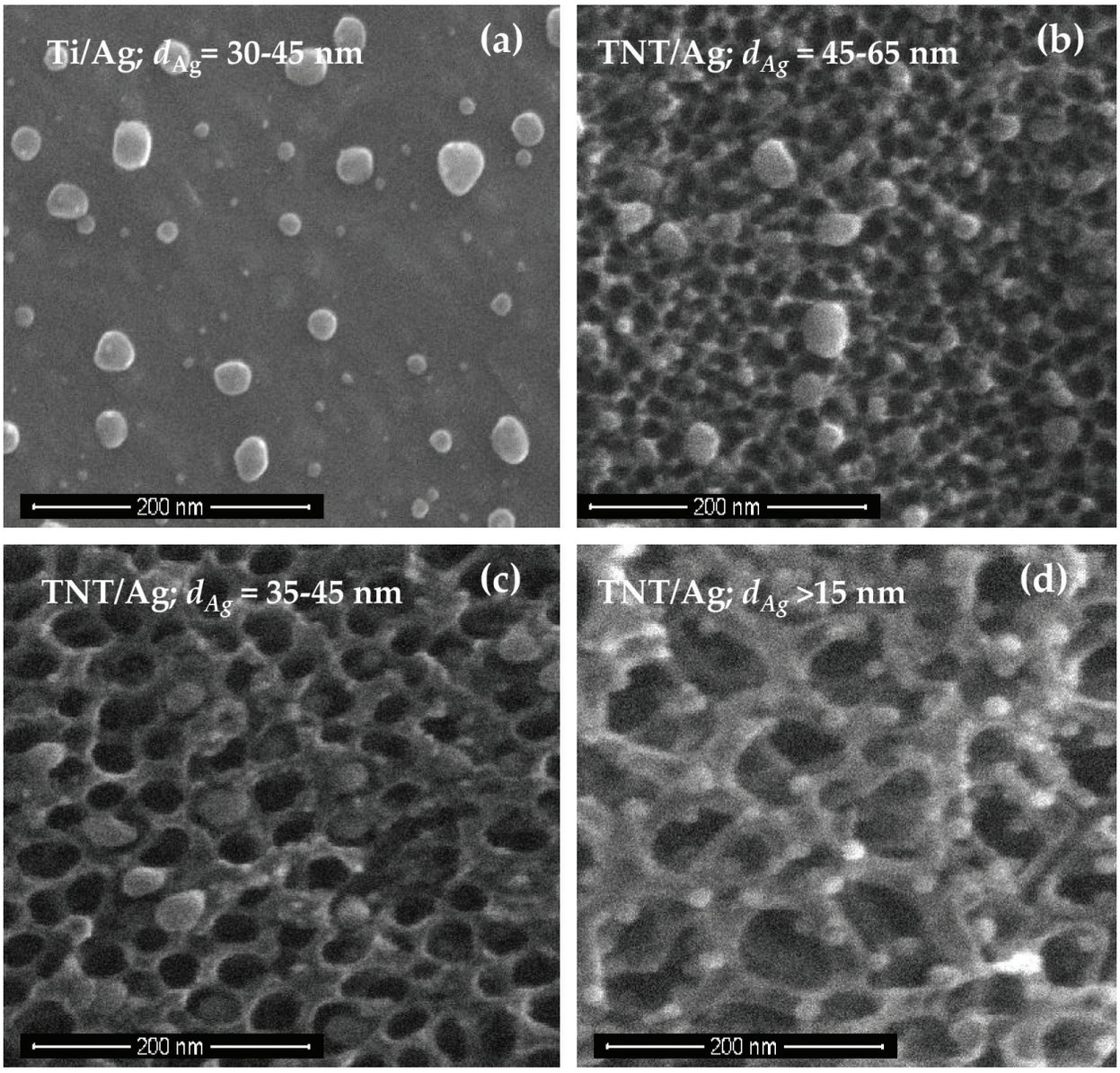


Figure 1. Scanning electron microscopy (SEM) images of titania nanotube coatings enriches with silver particles deposited by CVD method ((a) reference sample, (b) d_{TNT} = 23–30 nm, (c) d_{TNT} = 30–45 nm, (d) d_{TNT} = 80–150 nm) [46].

Summarizing this section, it can be stated that the CVD methods offer wide range of possibilities for the fabrication of silver-based materials with different morphology and structure. Moreover, the CVD method allows the formation of nanocomposite materials, in which the organic or inorganic matrix is enriched with silver nanoparticles. In this regard, the flame assistant technique, that is, FACVD, is especially useful [50]. However, TiO_2/Ag nanocomposities may also be fabricated in a one-step process, that is, direct-liquid injection metal-organic CVD (DLI-MOCVD) [51]. TiO_2/Ag materials may be also synthesized in the two-step classical CVD technique in which the titania nanocrystalline matrix is enriched with silver nanograins [52]. The above-mentioned methods allow the control of structure as well as the morphology of the TiO_2 matrix and the size of the synthesized silver particles.

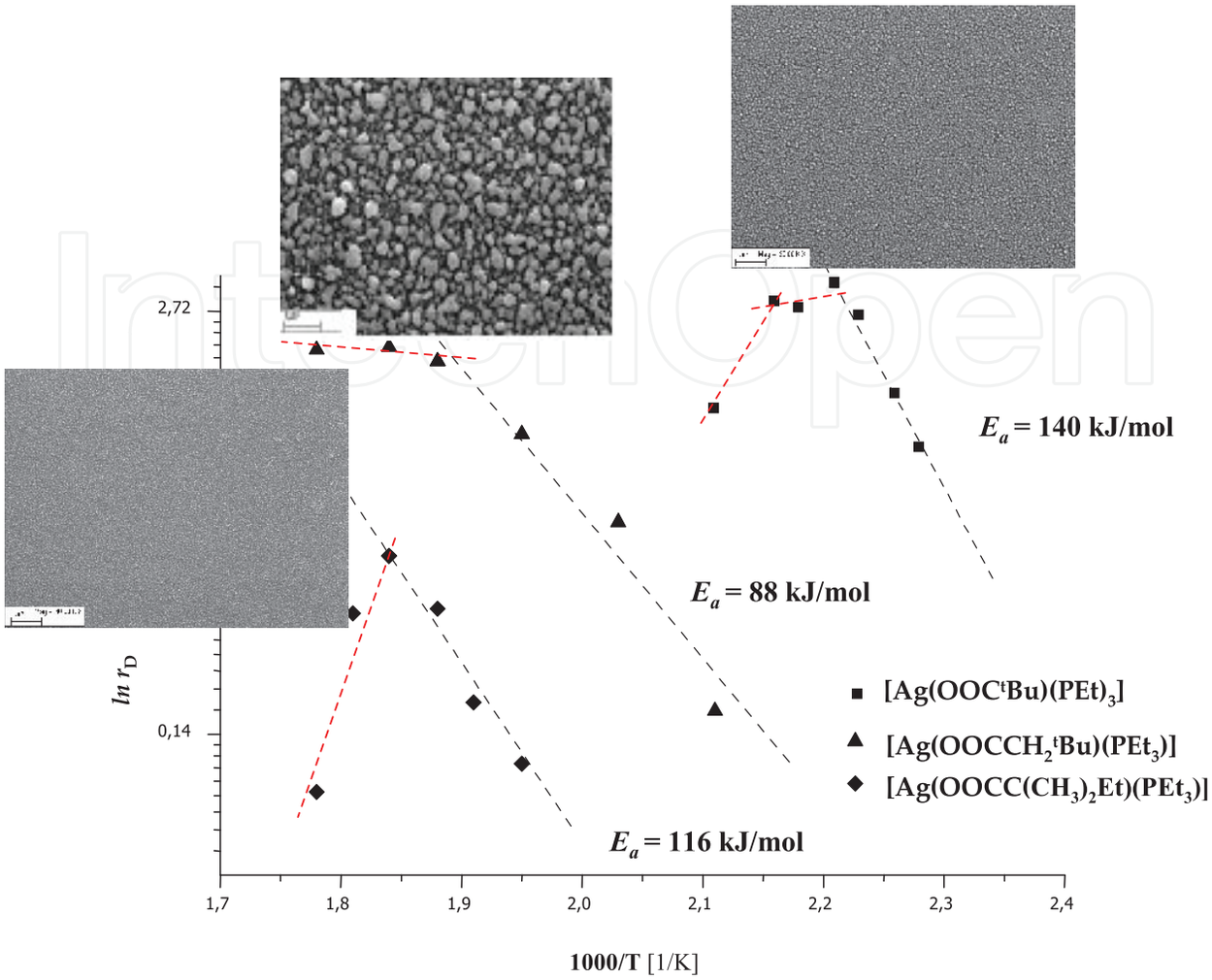


Figure 2. Influence of the carboxyl are groups on the morphology of silver layers, the deposition rate, and the value of activation energies (CVD technique, precursor [Ag(OOCR′)(PEt$_3$)]; R′ = –^{t}Bu (a), —CH$_2$^{t}Bu (b), and —C(Me$_2$)et (c)).

3. Atomic layer deposition

Generally, the atomic layer deposition (ALD) may be defined as a technique for the deposition of uniform conformal nanolayers by alternating exposures of a substrate surface to vapors of two precursors interacting in self-limiting reactions [53, 54]. Such reactions allow the same amount of material to be deposited on the whole surface. It provides excellent film uniformity even on large substrates. ALD technique enables controlling the film thickness at the atomic level and the layer-by-layer film deposition.

The interest in the use of ALD methods to obtain metallic silver materials (e.g. monolayers) is motivated in part by their use as catalysts in the oxidation of methanol to formaldehyde and in the epoxidation of ethylene [55]. The application of silver as an effective and relatively cheap antimicrobial agent in medical, cosmetic, and environmental technologies also led to the use of ALD techniques in these areas. According to previous reports, the following ALD techniques are used: (a) thermal ALD [56, 57], (b) plasma-enhanced ALD (PEALD [58–60]),

and (c) direct-liquid injection ALD (DLI ALD [61–63]). As in the CVD method, precursors are also the most important factor possessing a direct impact on the type of the produced material and the choice of deposition method. Considering the specificity of the discussed method, it should be noted that beside the chemical compound, being the source of the produced material (silver in this case), reducing agent must also be used. Such nature of ALD processes requires that precursors used in ALD techniques must exhibit greater chemical reactivity and lower deposition rate in comparison to CVD precursors. The silver precursors which are commonly used in ALD techniques are listed in **Table 2**.

Survey of literature reports shows that most of noble metals tend towards nucleation and grow as islands (Volmer-Weber growth mode) and many ALD cycles are required to obtain a continuous coating [64, 65]. This likely occurs because of the stronger interactions between metal atoms as compared to metal-substrate interactions leading to the formation of islands of metal nanoparticles on the substrate surface [66]. The good example is the deposition of silver film on the surface of the titania nanotubes (TNT) coating of tube diameters ca. d_{TNT} 30–65 nm (**Figure 3**) [58]. The dispersed AgNPs were deposited on the top edges of titania tubes after 25 ALD cycles. With increasing ALD cycles, the growth and the coalescence of particles were observed up to the formation of continuous metallic silver layer (after 150 ALD cycles). Moreover, results of our works revealed that the size of deposited AgNPs and their location on the surface of TNT layers significantly depend on tubes diameters [58]. The dependency between the sizes of silver particles deposited on the TNT layers of different tubes diameter confirms it (**Figure 4**). Obtained results revealed that the size of AgNPs, which were deposited on the surface of TNT coatings composed of dense packed tubes of the diameter d_{TNT} > 15–30 nm (d_{Ag} = 8–13 nm), was clearly larger in comparison to particles located on the surface of larger tubs (d_{TNT} = 30–80 nm, d_{Ag} = 6–10 nm). A similar effect has been observed for AgNPs deposited on TNT substrates using CVD technique [46]. The exchange of the substrate from titania nanotubes to titania nano-needles led to the necessity of increasing ALD cycles number from 25 up to 50, in order to obtain a layer composed of dispersed AgNPs [58]. It showed that the substrate-type also has an impact on the nucleation and the growth of nanoparticles.

Considering the results noted above, it can be stated that atomic layer deposition (ALD) is an excellent technique for the fabrication of both uniform silver nanolayers as well as dispersed

Precursor	ALD co-reactant	Deposition temperature T_D (K)	Technique	Refs.
[Ag(fod)(PEt_3)]	H_2; N_2-H_2	373–393	PEALD	[58–60]
[Ag(fod)(PEt_3)]	$BH_3(NHMe_2)$	383	ALD	[56]
[Ag(hfac)(1,5-COD)]	Propan-1-ol	383–423	DLI ALD	[61–63]
[Ag($OOCBu^t$)(PEt_3)]	H_2	413	ALD	[57]

fod: 2,2-dimethyl-6,67,78,8,8-heptafluoro-3,5-octanedionato; hfac: 1,1,1,5,5,5-hexafluoroacetylacetonato; 1,5-COD: 1,5-cyclooktadiene.

Table 2. Metallic silver precursors, which are commonly used in ALD techniques.

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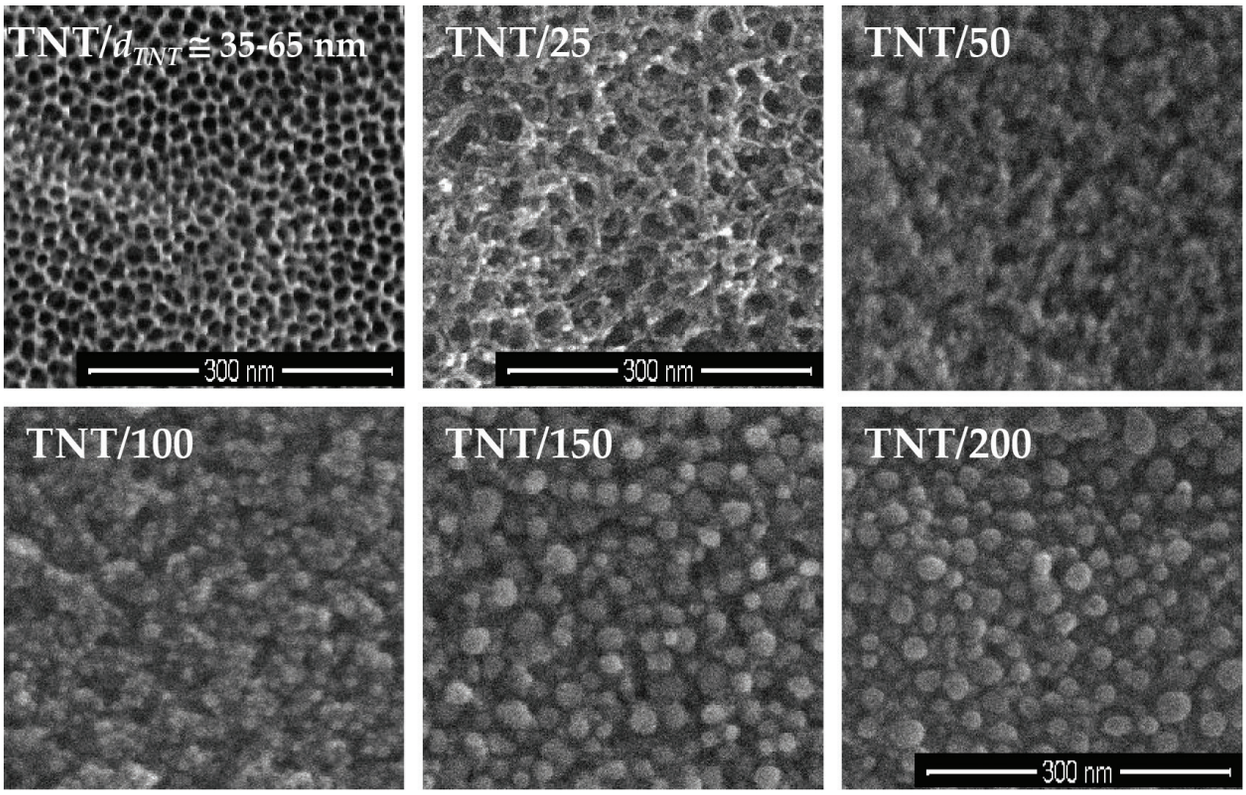


Figure 3. Silver nanoparticles deposited on the surface of TNT coatings after 25, 50, 100, 150, and 200 ALD cycles (PEALD; [Ag(fod)(PEt3)], H2; TD = 393 K; substrate Ti6Al4V/TNT; d_{TNT} = 30–65 nm).

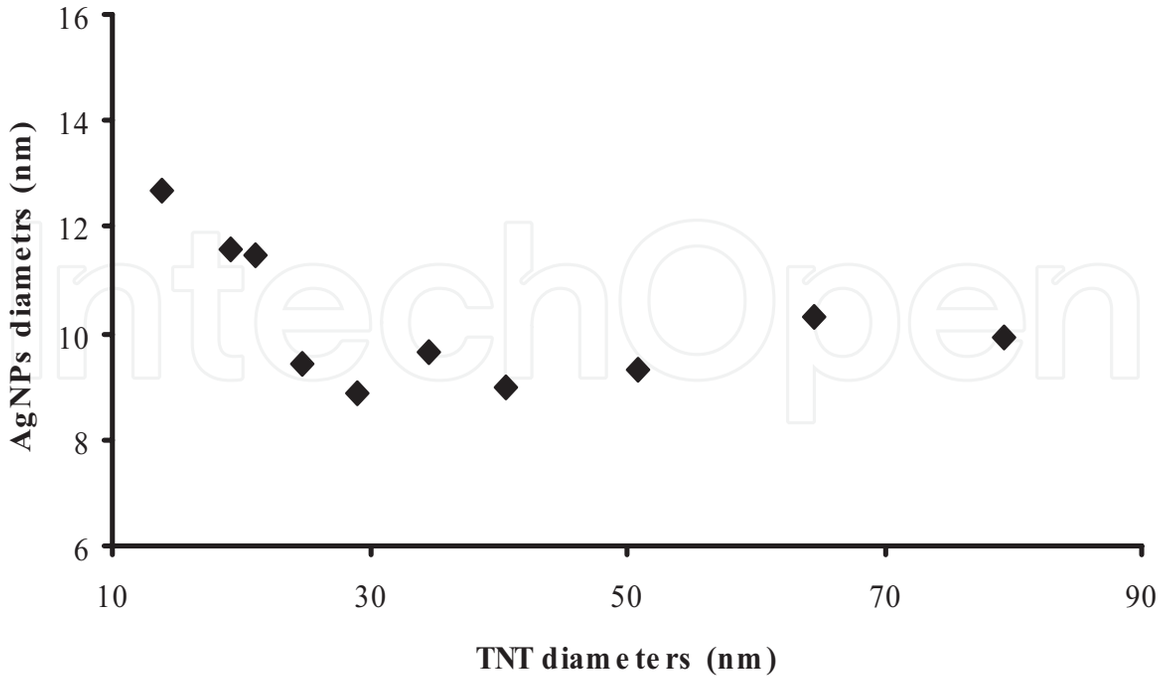


Figure 4. Effect of TNT surface morphology on the diameter of AgNPs after 100 ALD cycles on the surface of Ti6Al4V/TNT substrates.

silver nanoparticles on the surface of different substrates. The type of the precursor and the number of ALD cycles significantly affect the type of produced nanomaterial. The number of cycles allows controlling the nucleation and growth processes of nanoparticles on the substrate surface, which are important for the production of coatings composed of dispersed particles of the similar shape and size.

4. The silver ion release from the nanocomposite materials containing AgNPs

Silver is a widely used antimicrobial agent due to its effective biocide properties against a broad range of the bacteria, viruses, and fungus. This biocide activity of Ag-based materials depends on the release of silver ions (Ag^+) which is usually strongly bonded to biological molecules containing the electron donor groups, such as sulfur, oxygen, and nitrogen. The release of silver ions from the metallic layers of AgNPs and nanocomposite materials is due to the oxidation of metallic particles through their interaction with water molecules or body fluids. The release of Ag ions in a concentration level (0.1 ppb) capable of antimicrobial efficiency [67] and also their concentration below toxic level to human cells (10 mg/L) [31] should be taken into account during the design and the fabrication of silver-based materials intended for biomedical use. In studies concerning the strength of the antimicrobial activity of Ag-based materials, the amounts of the released Ag^+ from the material samples are mainly monitored in the phosphate buffered saline (PBS) solution at human body temperature (310 K) [30, 31, 67, 68]. The PBS solutions containing released Ag ions were analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES [68]), inductively coupled plasma mass spectrometry (ICP-MS [46, 58, 69]), inductively coupled plasma optical emission spectrometry (ICP OES [70]), or atomic absorption spectrometry (AAS [30]). Another method involves dissolving silver nanoparticles in nitric acid (e.g. 0.1 M), and then measuring the Ag^+ concentrations using atomic absorption spectrometry (AAS [71]) or anodic stripping voltammetry (ASV [72]).

Results of Zaho et al. [30] revealed that for the TNT/Ag system immersed in PBS solution, the concentration of silver ions after 5 h was close to 0.2 ppm and after 3 days increased up to 0.28 ppm and then remaining at this level for the next 4 days. Similar trends of the Ag^+ release were observed by Mei et al. [73] and Radtke et al. [58]; however concentration levels were different (1.4 and 0.015 ppm, respectively, after 30 days). By studying the release of AgNPs from wound dressings, Spange et al. [70] noticed the clear influence of the substrate type on this effect (AgNPs were deposited on bacteria cellulose, lyocell, and polyester/viscose textiles using atmospheric pressure plasma CVD method). The main reasons for the differences in silver release in this case were uneven swelling properties of each textile and differences in their surface areas. Holbrook et al. [74] suggest that different mechanisms are responsible for release of Ag^+ and AgNPs from wound dressings. The dissolution processes promote the release of silver ions, while AgNPs release can be caused by shear stress introduced by deformations of the solid-liquid-vapor triple line. This can be applied, for example, for better control of silver release from dressing and optimize its antimicrobial activity.

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For TNT/Ag coatings, in which silver grains were localized inside of TiO_2 tubes, we observed an interesting effect. For these materials after the first week, the concentration of the released Ag^+ in PBS solutions was 0.005–0.008 ppm, independent of silver amount deposited on the surface of TNT layer [46]. This concentration level decreased below 0.005 ppm after 21 days, and rapidly increased up to 0.020–0.022 ppm after 28 days. This effect may be explained by the location of the majority of AgNPs being inside of titania tubes and the oxidation difficulty related to particles' location. The concentration decrease of silver ions, which are released from the surface of TiO_2/Ag nanocomposite, is not an exception. Studies of Zhang et al. [69] of TNT/Ag and TNT/Ag-S nanocomposites revealed that after first 3 days, the concentration of silver ion release decreased from 0.25–0.35 pm to 0.05–0.03 pm and remains at this level for another 11 days. This effect was also noticed for Ag-DOPA-Ti materials (DOPA-Ti, dopamine-functionalized titanium surface) immersed in the PBS solution. Ag^+ concentration after 20 days of releasing was lower than 0.01 ppm [75]. Similarly for Ag ion-implanted titania nanolayers, the discussed effect was observed [33]. The studies of silver ion release from Ag-TiO_2(a) (a = anatase) revealed that concentration of Ag^+ increased in the first 8 days and after this time release rate decreased [72]. Explaining the mechanism of silver ion release, Akhavan et al. [72] assumed that the initial release process of Ag ions was generally controlled by water diffusion on the surface of the TiO_2 matrix. The easy water diffusion to the surface of silver nanoparticles, which were deposited on the titania nanolayer surface, resulted in the rapid release of the Ag^+ at initial stages. The later decrease in the release rate of silver ions can be explained by the ion release through the pores of the titania layer and the change of the release mechanism. This change in the behavior of the Ag ion released from the Ag-TiO_2(a) nanocomposite thin films is completely different from that in the bulk silver-based materials exhibiting a sharp increase in the ion release process [72]. The effect of the initial decline and subsequent rapid growth of the silver ions release rate from the polyamide/silver (PA/Ag) composites was explained by Kumar et al. [67] as a result both the rate of water diffusion and the physical changes in PA/Ag system. According to this report, it can be stated that the initial high release rate of silver ions is related to the oxidation processes of the silver particles located on the surface of the layer. For the Ag particles oxidation and the Ag + ions release from the interior part of the layer, water has to cross the diffusion barrier, which likely contains many crystalline lamellae. The diffusion of water molecules to the inter-lamellar regions can change the structural state, and in the consequence oxidize silver particles and lead to the migration of Ag ions from the interior part of the layer.

In summary, analysis of literature data shows that antimicrobial properties of silver-based materials are significantly connected with the release process of silver ions. This is important both for antimicrobial activity of these materials for a longer time and also for a safe dose of silver for human [30, 76].

5. Antimicrobial activity of silver films and silver-based nanocomposite coatings produced by vapor deposition technologies

Bacterial infections associated with the introduction of implants or other medical devices into the human body are one of the important problems of medicine. These infections

are the result of bacterial adhesion and contamination of implant/devices surfaces, which can cause serious complications in short and long term after the introduction/use. Antimicrobial activity of materials used in medicine is associated with the incorporation of components that locally can kill bacteria, fungus, and viruses or which can inhibit their growth without being toxic to the surrounding tissue at the same time. Silver is the component that is distinguished by the high activity against wide spectra of microorganisms in combination with low toxicity to human cells. Therefore, the modification of, for example, the surface of the implant by enrichment with AgNPs meets the above requirements. It is therefore understandable that extensive studies on applications of AgNPs in a number of areas are still ongoing although antimicrobial properties of silver have been known for a long time.

Experiments by Khalipour et al. [77] on animals revealed excellent *in vitro* antimicrobial activity of the Ag/SiO_xC_y coatings against *Staphylococcus aureus* (ATCC 6538), *Staphylococcus epidermidis* (ATCC 35983), and *Staphylococcus epidermidis* (DSM 18857) strains for at least 28 days. Moreover, results of ISO 10993-5 biocompatibility assay showed high biocompatibility of these materials and did not reveal any indications of cytotoxic effects. The antimicrobial property studies of AgNPs and CuNPs deposited on the surface of such biomedical materials as titanium, TiAlNb alloy, and steel (317 L), confirmed the high antibacterial activity of modified materials versus unmodified ones [78]. Moreover, the biocidal activity of both metallic particles increased with the increase of their amount on the substrate surface, independently of the substrate type. Results of these studies proved the better antibacterial properties of silver-modified materials in comparison to copper-modified ones. Yoon et al. [79] confirmed the good antimicrobial activity of AgNPs and CuNPs versus *Esterichia coli* and *Bacillus subtilis* strains. Simultaneously, they noticed that activity of both systems was associated with the particles size. The results of our works, concerning CVD of silver nanolayers on the surface of titanium implants used in maxillofacial surgery (**Figure 5**, **Table 3**) showed that bacterial sensitivity to AgNPs may be a feature of strains, which is independent of the morphological type and bacterial species [80]. The data presented in **Table 3** confirm that some strains belonging to the same species were characterized by different sensitivity to silver nanoparticles. The introduction of new technologies, for example, the selective laser melting technology, in the production of the new generation of implants, requires their enrichment with a coating which

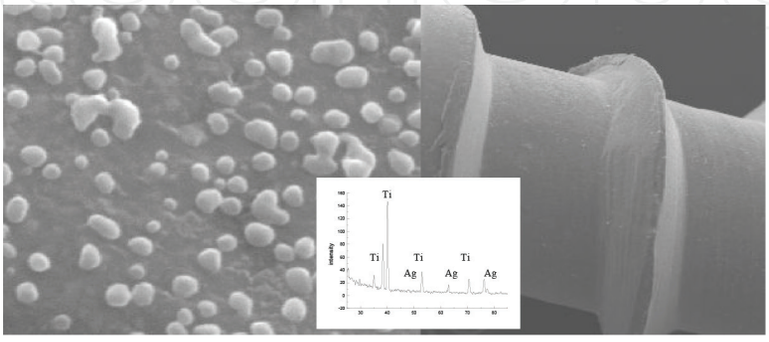


Figure 5. SEM images of silver nanoparticles deposited on the surface of the titanium screw, fixing the implant with the bone.

Bacterial strains	Bacterial count (CFU) after incubation on the surface of the silicon substrate (control sample)	Bacterial count (CFU) after incubation on the surface of the nanosilver coating (sample)	AE (%) percentage estimation of the antibacterial activity of nanosilver layers
Deinococcus radiopugnans	4.20×10^3	0	100
Burkholderia cepacia	1.70×10^4	0	100
Escherichia coli	1.24×10^3	1.46×10^2	88.2
Bacillus licheniformis	1.45×10^4	1.50×10^1	99.9
Staphylococcus lentus	3.15×10^3	2.80×10^3	11.1
Staphylococcus epidermidis C2	2.65×10^3	7.45×10^2	71.9
Tatumella ptyseos	7.30×10^1	0	100
Staphylococcus xylosus	6.20×10^2	0	100
Leuconostoc spp.	8.30×10^2	1.25×10^2	84.9
Staphylococcus epidermidis	8.16×10^2	0	100
Acinetobacter lwoffii	2.52×10^3	2.19×10^3	13.1
Pasteurella spp.	8.45×10^4	0	100
Pseudomonas luteola	4.20×10^3	0	100
Deinococcus grandis	9.30×10^4	0	100
Brevundimonas vesicularis	1.20×10^1	1.10×10^1	8.3
Gemella haemolysans C26	8.50×10^1	0	100
Streptococcus mitis	6.53×10^2	4.01×10^2	38.6
Bacteroides ovatus/thetaiotaomicron A23	1.45×10^3	1.53×10^3	0
Bifidobacterium spp.	5.30×10^3	0	100
Propionibacterium acnes	4.35×10^4	0	100
*Bacteroides ovatus/thetaiotaomicron NC*35	1.50×10^1	0	100
Gemella haemolysans C36	1.30×10^4	0	100
Fusobacterium necrophorum/ nucleatum D3	1.80×10^2	1.20×10^2	33.3
Fusobacterium necrophorum/ nucleatum D14	1.42×10^2	0	100

Table 3. Influence of silver nanoparticles on the selected aerobic, anaerobic, and relatively anaerobic bacteria, which have been isolated from the oral cavity and sites after the teeth extraction (the presented data are based on Ref. [80]).

will provide the appropriate bio-integration properties and antimicrobial activity. Studies of Devilin-Mullin et al. [81] on the deposition of silver nanolayers using ALD method on the surface of orthopedic implants produced by SLM technology are a good example.

Silver nanoparticles (size 40–90 nm) contribute to the clear growth reduction of a major osteolytic pathogen by *Staphylococcus epidermidis* on the implant surface, as well as to support the growth and differentiation of human cell lines important for bone regeneration. The interest in silver as an agent of countering bacterial infections dangerous to humans has greatly expanded the possibilities of its use. The application of the CVD technique to functionalize the wound dressings by their enrichment with silver particles has allowed obtaining a product with good antibacterial properties. A strong antibacterial effect against *Staphylococcus aureus* and *Klebsiella pneumoniae* strains even for low concentration of silver with coated wound dressing was reported by Spange et al. [69]. The risk of nosocomial infections has led to the development of research on the preparation of antimicrobial surface coatings on glass and ceramic tiles. Varghese et al. [39] revealed the promising properties of silver-silica coatings on the surface of above mentioned substrates produced by CVD technology. Results of these investigations showed that the standard test strains gave a $\log_{10} = 5$ reduction factor after 1-4 h, while more resistant methicicllin resistant *Staphylococcus aureus* (MRSA) was reduced by a $\log_{10} > 5$ after 24 h. This activity was maintained after simulated aging and washing cycles. Besides the aforementioned surface modifications of substrates (metallic, ceramic, or glasses) by metallic silver particles, nanocomposite coatings in which metallic or ceramic matrixes are enriched with AgNPs are also popular. The presence of silver particles in the structure of such materials can give them new properties or strengthen their anti-infection activity. The formation of the Ti/Ag composite on the surface of titanium substrates clearly inhibits adhesion of *Staphylococcus epidermidis* strains (ca. 42–55%) versus titanium as a reference sample, independently of the amount of incorporated silver (0.7–9%) [82]. Simultaneously, this type of composite significantly inhibits adhesion of *Klebsiella pneumoniae* strains (ca. 38–42%) for samples containing only 3–4% of silver. It suggests that bacterial sensitivity to silver depends not only on the type of strains but also on the amount of silver grains introduced to the composite. High antimicrobial activity of TiO_2/Ag layers produced by CVD method on the surface of glass substrates is another example worthy of highlighting [36, 50]. In this case, hospital-related pathogens were more resistant on AgNPs activity in comparison to usually tested bacteria strains, however their reduction to the 95–99.9% level was observed.

According to Mungkalasiri et al. [51], titania/silver nanocomposite coatings exhibit good antibacterial activity in the dark (*Staphylococcus aureus* strains, without the earlier UV activation), when they contain less then 1 at.% of silver.

Results of our works on TiO_2/Ag systems (**Figure 6**) show that besides the amount of incorporated AgNPs (ca. 1–4 wt.%), the polymorphic structure of the titania matrix may also significantly influences their antimicrobial properties [52]. The best activity against the *E. coli* strain was observed for TiO_2 anatase/rutile coatings (94–100% mortality of *E. coli*). The pure anatase layer exhibited weaker biocide properties (only 47% mortality). However, the enrichment of the TiO_2 anatase layer with ca. 4 wt% of silver caused significant increase in its activity up to 99.9% (mortality).

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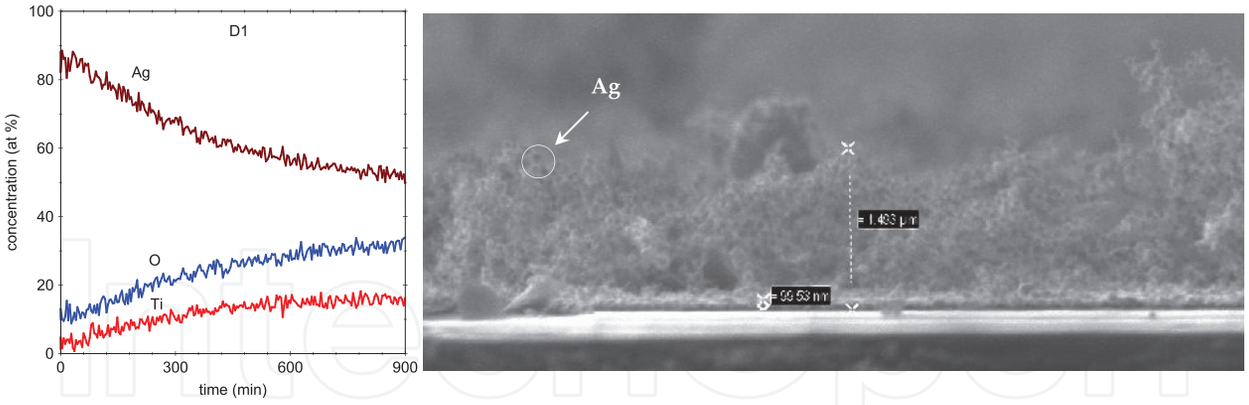


Figure 6. SEM images and XPS depth profile of the TiO_2/Ag composite coating deposited on the surface of titanium implant (CVD, titania matrix were obtained using $[Ti_6O_6(H_2O)_2(O^iBu)_6(OOC^tBu)_6]$ as the precursor, T_D = 713 K, p = 3 hPa, t =60 min, Ar, and silver nanoparticles were deposited using $[Ag(OOCCH_2{}^tBu)(PEt_3)]$ as the precursor, T_D = 433 K, p = 1.5 hPa, t = 60 min, Ar) [52].

Also Li et al. [83] who investigated the biocide activity of titania nanotubes (TNT) and TNT/Ag, have taken into account the above mentioned dependency. The antibacterial efficiency of TNT coatings was observed to change in the order of anatase > rutile > amorphous. In all the studied cases, TNT/Ag system yielded the best antimicrobial activity. Studies on TNT and TNT/Ag materials both in the dark and under the UV light revealed that beside the incorporation of ca. 10 nm silver particles into titania tubes, the tube diameter is also an important factor which significantly influences the antibacterial properties of these systems [30]. Obtained results showed that antimicrobial activity of coatings composed of d_{TNT} = 100 nm tubes was better than that for layers composed of d_{TNT} = 75 and 50 nm ones. In our investigations, we have focused on bioactivity studies on TNT/Ag nanocomposites produced by the enrichment of TNT coatings with AgNPs using CVD and ALD methods [46, 58]. Independently of the applied method, the best antibacterial activity was noticed for systems composed of TNT tubes of diameter lower than 25 nm and decorated by silver particles localized on the top edges of tubes. This can be explained in terms of the synergy of two effects: (a) properties of TiO_2 layers composed of small diameter tubes, which support inhibition of the bacterial biofilm development [84, 85] and (b) the presence of Ag particles deposited on the TNT layer surface. The latter factor is associated with the strong antimicrobial activity of silver particles resulting in the direct interaction AgNPs-bacteria and the release of silver ions in the water environment. Brennan et al. [86] reported that silver-containing hydroxyapatite coatings (Ag-HA) give better efficiency as biocidal agents (against MRSA) in comparison to uncoated HA coatings. The studies of titanium plates covered by Ag-HA and HA coatings and implanted subcutaneously in the backs of rats confirm it.

In concluding this section, it is important to note that despite extensive research into the biocidal activity of silver, both as nanolayers and as nano-particles, the exact mechanism of this process is not yet completely understood. This is due to several factors (e.g. particle

size and shape, stability, crystallinity, and reactivity) that can affect this activity at the same time. Among the mechanisms of these processes, which are proposed in literature [87–89], the most comprehensive is the one proposed by Marambio-Jones and Hoek [90]. The postulated mechanism assumes that silver antimicrobial activity can result from: (a) up-taking of free silver ions followed by distribution of ATP production and DNA replication; (b) generation of reactive oxygen species (ROS) by Ag nanoparticle and Ag + ion; and (c) penetration of Ag nanoparticles through damaged cell membranes. A more detailed mechanism has been proposed by Naidu et al. [91] containing several steps: (a) the attachment of silver nanoparticles to the cell membrane and also penetration inside the bacteria; (b) the interaction of silver ions with bacterial membranes, which contain sulfur-containing proteins as well as with phosphorus-containing compounds like DNA; (c) attack on the respiratory chain in bacterial mitochondria leading to the cell death; and (d) the release of Ag ions inside the bacterial cells (in an environment with lower pH), leading to the formation of free radicals and inducing the oxidative stress.

Our analysis of literature data suggests that silver materials (nanoparticles, nanolayers, and nanocomposites) give good bactericidal activity even at very low concentrations. According to postulated mechanisms, this activity is due to the ability of bacterial cells to absorb and concentrate Ag ions. The antibacterial efficiency of silver particles depends both on the morphological differences that exist between the bacteria, as well as on the particles size, their location on the substrate surface and the reactivity.

6. Bio-integration properties and toxicity of silver-based materials

Capabilities of CVD and ALD techniques enable the fabrication of materials containing silver nanoparticles of different size, shape, and reactivity, which can be designed to make them suitable for specific biomedical applications. Despite extensive studies, investigations of problems such as materials bio-integration, their anti-inflammatory properties, and toxicity are still being carried out. According to Dobrovolskaia and McNel [92], these studies can be separated into two following categories: (1) response of nanoparticles which are specifically modified to stimulate the immune system and (2) undesirable side-effects of other nanoparticles. Zhang et al. [93] observed the formation of fibroblasts on the surfaces of studied samples investigating cytotoxicity of Ti-MAO-Ag layers (MAO—microarc oxidation, the 3 T3 cell colony formation). The slight differences in fibroblasts morphology on the surface of layers with and without silver indicated the similar bio-compatibility of Ti-MAO-Ag and Ti-MAO systems. Moreover, no cytotoxicity of these materials has been found. Studies of bactericidal activity and biocompatibility (*in vitro* and *in vivo* investigations) of TNT/Ag coatings (silver was implanted into TNT layers by plasma immersion ion implantation (PIII) method) revealed that despite excellent antimicrobial efficiency of systems in which silver particles were localized on the TNT layer surface, their biocompatibility was impaired [73]. On the other hand, the deposition of most silver particles on the walls (inside of nanotubes) resulted in an improvement of the biocompatibility of TNT/Ag systems. However, it was comparable to TNT coatings not enriched with Ag nanoparticles. The results of cyto-compatibility

studies of rat calvaria osteoblasts on the surface of TiN/Ag films confirmed also their good biocompatibility [94]. The lack of significant differences between biocompatibility of TiO_2/Ag layers and uncoated titanium surface was noticed by Chang et al. [95] (MTT assay of human gingival fibroblast (HGF)). Studies on the L929 murine fibroblast adhesion (measured after 24 h) and proliferation (assessed after 72 h) on the surface of Ti/Ag and TNT/Ag coatings (containing AgNPs deposited by CVD technique) revealed clear influence of silver particles presence on the biocompatibility of these materials [46]. In all cases of TNT/Ag layers, the adhesion of cells and proliferation were significantly better than that in the case of uncoated titanium surface. The size, amount, and location of AgNPs on the surface of TNT substrates seem to decide the biocompatibility of studied coatings. In the case of TNT/Ag materials incorporated by ALD silver particles (produced on the surface of Ti6Al4V samples), the better adhesion and proliferation of fibroblast cells in comparison to uncoated sample of Ti6Al4V were also noticed [58]. Analysis of presented data showed that the results concerning biocompatibility properties of silver nanolayers and nanocomposites containing AgNPs were not clear and required further work on this topic. This fact makes necessary studies on the adhesion and proliferation of various cells, with the use of multifarious deposition/incorporation AgNPs methods and with the use of nanoparticles of different size, stability, and structure.

The strong antimicrobial properties of materials based on silver nanoparticles or layers, which have been reported by many investigators, have led to interest in their applications in different medical fields, especially in implantology. Research on their toxicity is therefore essential. According to literature data, AgNPs are cytotoxic for several types of cells; for example, human peripheral blood mononuclear cells, human alveolar macrophage cell line, neuroendocrine cells, rat liver cell line, and mouse germline cells [86, 91]. The mechanism of toxicity has not been clearly explained. However considering the earlier reports it may be associated with the ionization of silver ions in the cells, which can lead to changes in the permeability of the cell membrane to both potassium and sodium, interaction with mitochondria, and induction of the apoptosis path via the production of ROS which leads to cell death [91]. Based on previous research, we can assume that the concentration and size of silver nanoparticles are the main factors affecting their cytotoxicity. Milić et al. demonstrated that in spite of a significant uptake into the cells, AgNPs had only insignificant toxicity at concentration lower than 25 mg/l, whereas Ag^+ exhibited a significant decrease in cell viability at 1/5 of this concentration [96]. The results of Comet assay, according to Brennan et al. [86], the concentration of AgNPs higher than 10 μg/g revealed the cytotoxicity effect on primary human mesenchymal stem cells and osteoblasts. Low toxicity or lack of toxicity for silver nanoparticles of diameter c.a. 20 nm was noticed both for colloidal nanoparticles (negative zeta potential), Ag-montmorillonite nanocomposite, and also Ag-DOPA-Ti (DOPA-Ti = titanium substrate coated with poly(dopamine) [75, 97, 98]. However, AgNPs of diameters ca. 24 nm showed cytotoxic activity to macrophages, causing a pro-inflammatory response and apoptosis [86]. Based on previous reports, the lack of clear results concerning silver nanoparticles toxicity to human should be emphasized. It may be associated with the relatively short-time of experiments and also with the fact that most of them are based on *in vitro* cellular studies [91].

7. Concluding remarks

Despite relatively small amounts of literature reports concerning the use of chemical vapor deposition (CVD), and atomic layer deposition (ALD) techniques in the production of biomedical materials, both methods reveal large possibilities in this regards. The most important advantage of these methods is the possibility of controlling the production of different materials based on silver on substrates of different shape, surface morphology, and structure. According to the type of used precursor and the deposition conditions (deposition temperature, time, and deposition rate), it is possible to produce the uniform silver nanolayers, dispersed silver nanoparticles (AgNPs) or their aggregates, and nanocomposite coatings enriched with silver nanoparticles. Through the control of the nucleation and growth conditions of nanoparticles, it becomes possible to direct the size of deposited AgNPs, their structure, stability, purity, and their location on the substrate surface. Thus, it becomes possible to optimize physicochemical properties and bioactivity of the produced materials. From the biomedical point of view, the ability of silver nanoparticles to ions release is the important topic. It may happen that the material containing even the low amount of silver nanoparticles reveals high biocide activity because of large amount of released Ag^+. The use of CVD and ALD techniques creates opportunities to the incorporation of AgNPs to substrates of a complex shape and also to the formation of ceramic or polymeric composites enriched with silver nanoparticles. The placement of AgNPs inside the matrix may lead to the process of releasing of silver ions over longer periods of time. Such procedure results in the material of optimal microbicidal activity (spread over the time) and simultaneously reduces the cytotoxicity of this material by decreasing of the amount of silver ions released. It is likely that silver-based materials obtained using above-mentioned techniques may be widely and safely used as a biocide agent not only in biomedical and cosmetic technologies but also in the food and textile industry.

Silver nanoparticles and silver-based materials are one of the most attractive materials for variety of applications. In this chapter, we have provided comprehensive review of synthesis methods, antimicrobial properties, and cytotoxity of Ag-based nanomaterials. Releasing of silver ions (mainly responsible for the toxicity of silver) from AgNPs and silver-based products has been especially emphasized. It was felt necessary to put together detailed data about both the positive as well as negative aspects of silver-based nanomaterials in order to outline their potential safe applications, especially in biomedical technologies and in advanced environmental treatments (air, water, and surface disinfection). AgNPs and AgNPs-based nanomaterials can be used as safe antimicrobial products only if their toxicity will be on the optimally low level. Using the techniques, which provide the strict control on the size, shape, concentration, and location of AgNPs on the surface (like CVD and ALD), it might be possible to produce wide group of innovative Ag-based nanomaterials with tremendous antibacterial properties without noticeable risk to humans or the environment.

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