

Surface Segregation in Ag/TiO_x 3D Nanocomposite Prepared by Physical Vapor Deposition

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Abstract. The antimicrobial activities of silver based nanocomposites are usually studied in terms of Ag content and ion release rate. Under this condition, controllable silver ions release with high antibacterial activity is the basis for silver based nanocomposite. The goal is to investigate the influence of O₂ content and titanium oxide barrier thickness on the evolution in morphology. The SEM/TEM results showed that the size of Ag nanoparticles has a clear dependence on O₂ concentration in reactive sputtering process; increased oxygen implies larger Ag nanoparticles in the matrix. In addition, a clear suppressing effect and better size distribution is obtained after the thickness of coated titanium oxide barrier is verified.

1. Introduction

3D nanocomposite thin films consisting of noble metal nanoparticles embedded in a transparent and non-toxic matrix such as titanium oxide, have received increasing attention because when these features are combined with the size-tunable optical, electronic and antibacterial properties of nanoparticles, the possibilities are wide [1]. Titanium oxide has been recognized as a well-matched biomaterial matrix, and various techniques can be applied to modify the surface properties for large range of use [2]. They show considerable promise in biomedical applications, where device surfaces are required to be biocompatible, as well as mechanically and chemically stable. An antimicrobial property of titanium oxide is also a beneficial characteristic of biomedical devices, as many clinical studies have reported that bacterial infection after implantation is a significant complication [3–5].

Silver as a noble metal is well known as one of the most interesting antibacterial materials because of its excellent broad spectrum antibacterial activates and they can come in a variety of shapes and sizes [6–9]. The antimicrobial activities of silver based nanocomposite are usually studied in terms of Ag content and ion release rate. Silver ions has been reported to interact with nucleic acids and cytoplasmic components and to bind bacterial cell membrane, in addition, due to interaction between the silver ions and DNA structure, respiratory chain enzymes of bacterial their multiplication would be prevented [10–12]. Under this condition, controllable silver ions release with high antibacterial activity is the key point of silver based nanocomposite.

Many way can be used to produce these nanocomposites thin films such as chemical synthesis, ion implantation, magnetron sputtering and others. The magnetron sputtering methods including RF sputtering and DC reactive sputtering have been widely used due to its flexibility, simplicity in the materials combination and tailoring in size distribution. RF-sputtering is one of the most feasible way



because of the capability of obtaining an homogeneous surface coverage at low temperatures [13], however, Comparing with the relative lower deposition rate and simple morphology of RF magnetron sputtering, DC reactive magnetron sputtering is attracted intense interest not only provides controllable structures, sizes and morphologies flexibility and in forming the films with controllable stoichiometry, but also is straightforward to implement in industrial-scale production for the relative high deposition rate and large area coated[14-16].

In this work, varied nanocomposited of titanium oxide thin films containing Ag nanoparticles were synthesized on commercially pure Si, quartz and glass substrates by a DC reactive magnetron co-sputtering method with varied O₂ partial pressure, moreover, RF magnetron sputtering was also selected to serve as a non-oxygen model for comparing.

2. Experimental

The nanocomposite coatings were prepared in a home made deposition vacuum chamber by reactive co-sputtering of Ti target and Ag target from two independent magnetron sources. The base pressure is 10⁻⁸ mbar, and O₂/Ar were 1.6% and 16%, a pulse box also used when 16% to avoid arc and target poisoning. Ti target (99.99%, Goodfellow GmbH) was sputtered by a DC planar magnetron source (ION'X 2UHV, Thin Film Consulting) and the Ag target (99.99%, Goodfellow GmbH) by a RF magnetron source (ION'X 2UHV, Thin Film Consulting). Both continuous and independent monitoring of the deposition rates of the Ag and TiO₂ were done in situ by using the two quartz-crystal monitors. The deposition rates were monitored independently for Ag and Ti with quartz-crystal microbalances and by variation of the power applied to the magnetron sources the silver metal volume fraction (MVF) was controlled. The sample holder was rotated throughout the deposition process to achieve uniform and homogenous deposition on all the samples mounted on the sample holder. First, a titanium oxide buffer layer with a thickness of 10 nm was deposited to increased adhesion strength and relax the stress between substrate and coatings. After that, the silver containing titanium oxide nanocomposite (30 nm in thickness) was fabricated with the rotation rate of a substrate holder at a constant rate of 9 rpm. Next, A varied titanium oxide in different thickness was produced for adjusting silver ion release and morphology. Meanwhile, A set of same structure samples were prepared by co-sputtering of TiO₂ ceramic target (99.9%, Williams Advanced Material) and Ag target (99.99%, Goodfellow GmbH) as reference of producing in a pure argon atmosphere.

3. Results and Discussion

3.1. Oxygen dependence

SEM images clearly show these nanocomposite surface morphology, including the silver nanoparticles on the surface region via different oxygen content (Fig. 1(a)–(c)). Fig. 1a is a typical image without oxygen influence which is consistency with TEM. However, Ag nanoparticles were irregularly sized and agglomerated after introducing oxygen, from a few nanometers to hundreds of nanometers. We can conclude that the larger Ag nanoparticles existed not only in the matrix but also on the surface. Ag islands and "nodules" were even formed in 16% O₂ because of surface energy. It was reported that the physical mechanism of Ag agglomeration was related to the surface diffusion of Ag atoms which are driven by surface energy, resulting in the grain boundary grooving, hillocks formation, and, finally, agglomeration.

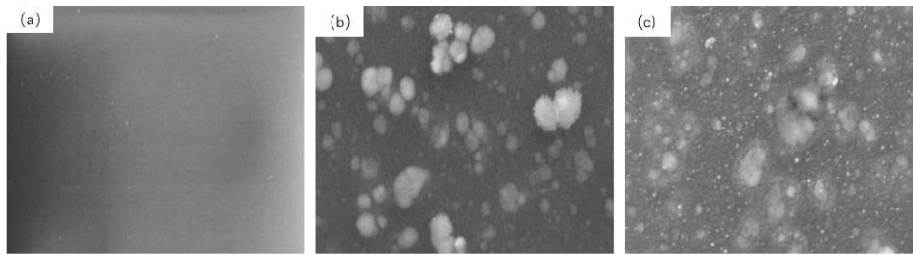


Figure 1. SEM images of 15 vol% Ag-TiO₂ nanocomposites prepared with different oxygen partial pressure (a)non-reactive sputtering and without oxygen(b) oxygen partial pressure 1.6% (c) oxygen partial pressure 16%

To study the size of the silver nanoparticles in the Ag/TiO_x nanocomposites, TEM analysis was utilized. Fig.2 shows TEM image of the silver nanoparticles with different O₂ concentration. We can see that the Ag nanoparticles are rather small with diameters around 2 nm and distribute quite well in Fig. 2a which produced without oxygen(RF magnetron sputtering). However, the particle size of Ag Nanoparticles growing bigger after oxygen was introduced which increase to 5-10 nm. And we can see clearly from the TEM picture that more oxygen means larger Ag nanoparticles in the matrix.

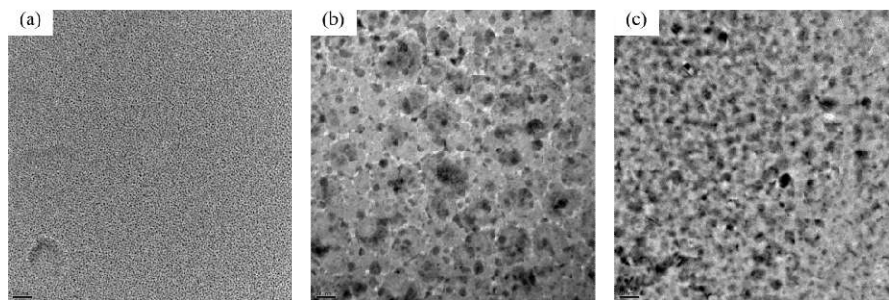


Figure 2. SEM images of 15 vol% Ag-TiO₂ nanocomposites prepared with different oxygen partial pressure (a)non-reactive sputtering and without oxygen(b) oxygen partial pressure 1.6% (c) oxygen partial pressure 16%

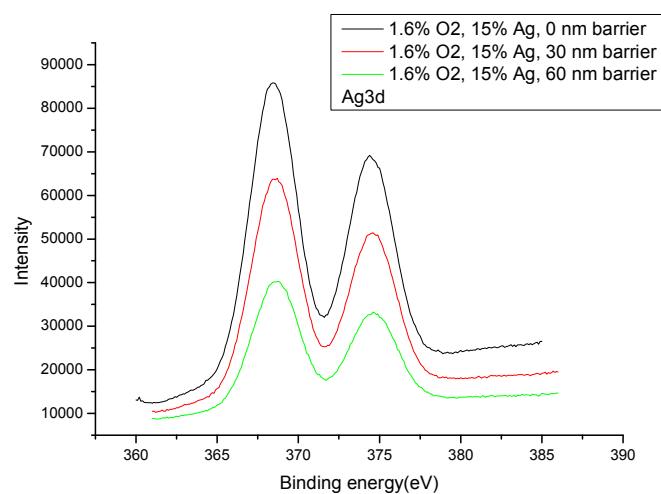


Figure 3. XPSspectra of 15 vol% Ag-TiO₂ nanocomposites prepared with oxygen partial pressure at1.6%

3.2. Barrier layer impact

Figure 3 shows the X-ray photoelectron spectra of the evolution of Ag 3d core levels depends on the barrier thickness during deposition at the surface (1.6% O₂). The decrease of intensity only between 1-2 times which indicates that still metallic silver appears on the surface due to the aggregation that still some big ones appears on the surface. Similar results can also be observed from the SEM images (not showed here)

4. Summary

The Ag/TiO₂ composite thin films were deposited by reactive magnetron sputtering. The morphology of Ag/TiO₂ composite thin films were studied by using X-ray diffraction, scanning electron microscopy, transmission electron microscopy, X-ray photoelectron spectra and atomic absorption spectrometry. The results show that silver nanoparticles in thin film bulk phase and surface aggregation and irregular distribution of the surface increased with the increase of oxygen flow rates. The buffer layer on the inhibitory effects of silver nanoparticles surface segregation is limited.

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