INVESTIGATION OF BIMETALLIC W/CU NANOPARTICLES PRODUCED BY A GAS AGGREGATION SOURCE USING A SEGMENTAL TARGET

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Abstract

In this work, we consider the possibility of obtaining bimetallic W/Cu nanoparticles (NPs) by means of a magnetron-based gas aggregation source (GAS) of NPs. For this, a GAS of original construction was equipped with a segmental target consisting of two metals: tungsten and copper. The properties of prepared bimetallic W/Cu NPs, namely their morphology, chemical structure, optical properties, and the antibacterial action of produced W/Cu NPs are subsequently studied.

Keywords: Gas aggregate sources, magnetron sputtering, W/Cu nanoparticles, antibacterial properties

1. INTRODUCTION

Tungsten-copper compounds are pseudo-alloys composed of distinct particles, since the W and Cu are mutually insoluble, i.e., they do not form a solution or intermetallic compounds. Because of this, the microstructure W/Cu is rather a metal matrix composite instead of a true alloy [1-3]. These materials have excellent thermal, electrical, and mechanical properties such as high hardness and strength, a low thermal expansion coefficient, good arc resistance arising from W, and high electrical and thermal conductivity from Cu. Due to this W/Cu composites are widely used in various fields such as sintering metallurgy, microelectronics, aerospace, biomedical applications, etc. [1, 4]. In addition, the functional properties of W/Cu may be in some cases even enhanced when W/Cu is produced in the form of nanoparticles (NPs).

Although there exist numerous strategies for the production of such NPs that are based on chemical synthesis [5-7], in this work we consider the possibility of obtaining bimetallic W/Cu NPs by means of a magnetron-based gas aggregation source (GAS) of NPs, i.e., by purely physical, solvent- and linker-free process, which is based on the condensation of the metallic supersaturated vapors produced by a magnetron discharge in an inert gas flow [8-10]. As the production of single-phase NPs using GAS deposition systems is relatively well-understood, the possibility of synthesizing two-component NPs remains still subject of intensive ongoing studies. In principle, three principal strategies may be followed. The first one is based on in-flight coating/decorating of single material NPs on their way between an aggregation chamber and a substrate (e.g. [11]). The spatiotemporal separation of the core and shell formation provides excellent control over the deposition process but at the cost of relatively thin shells or even incomplete coating of the cores that can be limiting in some of the applications. The second possible approach relies on the use of two (or even more) magnetrons inserted into a single aggregation chamber [12,13]. In this case, however, due to limited diffusion length at high pressure necessary for the particle formation, not only bi- or multi-material NPs are formed, but also a significant portion of single-material NPs is produced as well. This drawback can be overcome by the third strategy which utilizes a single magnetron equipped with a segmental target composed of two materials. Different concepts that employed different target configurations/geometries were studied including metallic

wires introduced into the erosion zone of a planar target manufactured from another metal [14], cylindrical-post magnetrons with a metallic strip mounted onto a cylindrical target from another metal [15] or by a bi-metallic target, where the second material is introduced in form of pellets into the erosion of planar magnetron [16]. The aim of this study is to demonstrate that the latter approach is applicable for the effective production of W/Cu NPs as well as to provide their characterization from the point of view of their morphology, structure, optical properties, and antibacterial activity.

2. MATERIALS AND METHODS

The W/Cu NPs were produced using a deposition system schematically depicted in **Figure 1**. The sputtering took place in a stainless, water-cooled GAS. The planar magnetron was made of a segmental target consisting of two metals - tungsten and copper - and was powered by a direct current power supply. The sputtering was carried out in Ar at the pressure of 40 Pa in the aggregation chamber and magnetron current of 300 mA. The aggregation chamber was attached to a main vacuum deposition chamber and the whole set-up was pumped by scroll and turbo-molecular pumps.

The W/Cu NPs were deposited onto substrates (Si substrate, Microscope slides (glass), polypropylene (PP) meshes (provided by Goodfellow; nominal aperture 125 μm; monofilament diameter 110 μm) introduced into the main deposition chamber through a load-lock system.

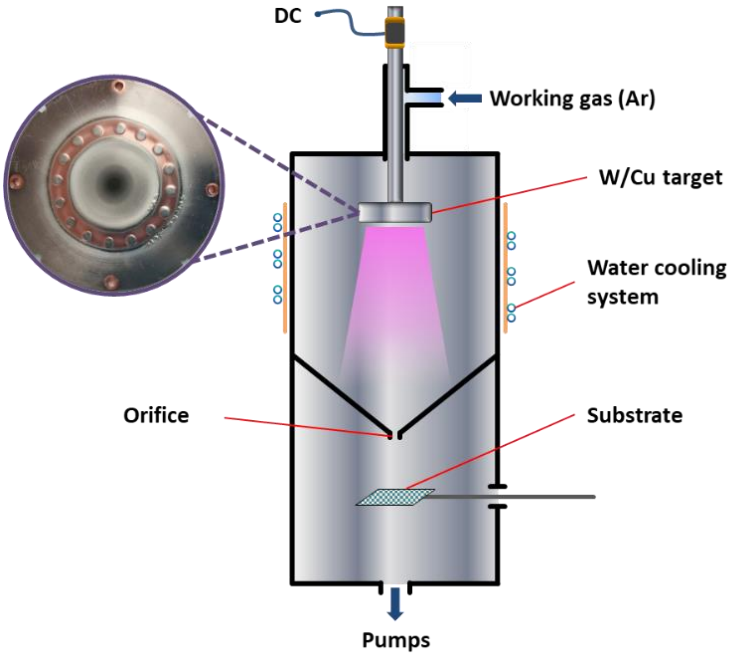

Figure 1 Schematic of the magnetron sputtering system with GAS and photo of the segmental target (left)

The morphology, size and structure of deposited NPs were investigated by scanning electron microscopy (SEM; JSM-7200F, Jeol). The SEM images were acquired in both secondary and back-scattered electron modes. The chemical composition was determined using energy-dispersive X-ray spectroscopy (EDX; JED-2300, JEOL). The optical properties were evaluated by UV-Vis spectrophotometry (Hitachi U-2900).

The release of Cu and Ag ions was measured by atomic absorption spectroscopy (AAS, SensAA Dual, GBC Scientific Equipment Pty Ltd.). The samples were put into the 24-well plate. Each well was filled with a medium of 1% Luria Broth (LB) in phosphate buffer saline (PBS) and analyzed after a given incubation time. Antibacterial properties against Escherichia coli Seattle 1946 (ATCC 25922) were measured using the counting of colony-forming units (CFU) method.

3. RESULTS AND DISCUSSION

The first step of this study was the evaluation of the morphology and structure of produced W/Cu NPs. As shown in **Figure 2a**, the formed NPs have a relatively narrow size distribution with sizes ranging from 15-20 nm. Furthermore, the comparison of SEM images acquired simultaneously in secondary (SE) and back-scattered (BE) electron modes revealed significant differences in the sizes of detected NPs (**Figure 2b**). This apparent discrepancy is due to the different principles of the SE and BE imaging modes; while the SE images provide information about the morphology of the measured NPs, BE imaging is more sensitive to the material, with a more intense signal for heavier elements. The observed difference between SE and BE SEM images thus suggests the core-shell structure of produced NPs with W core and approximately 2.5 nm thick Cu shell.

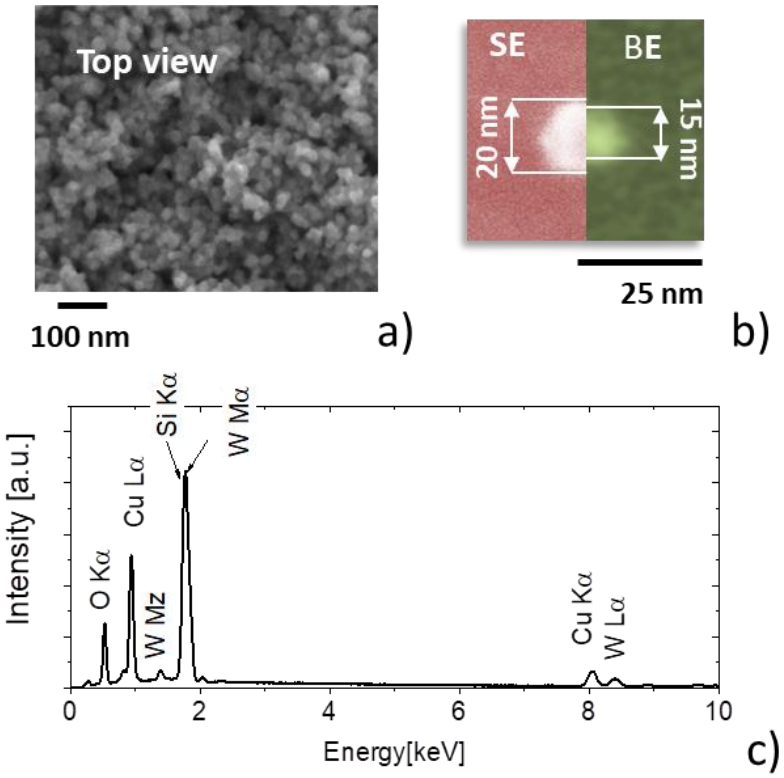

Figure 2 a) SEM image of W/Cu NPs film. b) Comparison of SE and BE SEM images of single W/Cu nanoparticle. For better clarity, false colors are used. c) EDX spectra of W/Cu NPs film

The bi-metallic character of the produced NPs was further confirmed by EDX (an example of EDX spectra acquired for NPs film deposited for 10 minutes is presented in **Figure 2c**). According to these measurements, the Cu/W atomic ratio is approximately 1.6. It is worth noting that besides peaks that correspond to W and Cu, EDX also revealed the presence of Si and O. While the presence of Si is due to the substrate material, the appearance of O in the EDX spectra suggests significant oxidation of NPs when exposed to air during the transfer from the deposition chamber to the SEM/EDX.

The investigation of the cross-sections of W/Cu NPs films by SEM/EDX revealed other two important facts concerning the deposition rate and structure of the deposits. As can be seen in **Figure 3a**, where an SEM image of the cross-section of the film deposited for 10 minutes is presented, the deposition rate under the experimental conditions used in this study reaches a value of 100 nm per minute and the resulting coating exhibits a high level of porosity. The latter is consistent with results obtained with single-material NPs films deposited using a similar deposition system [17]. The second important fact is the same depth profile of Cu and W, as indicated by EDX mapping (**Figure 3b**) which confirms the stability of the deposition process.

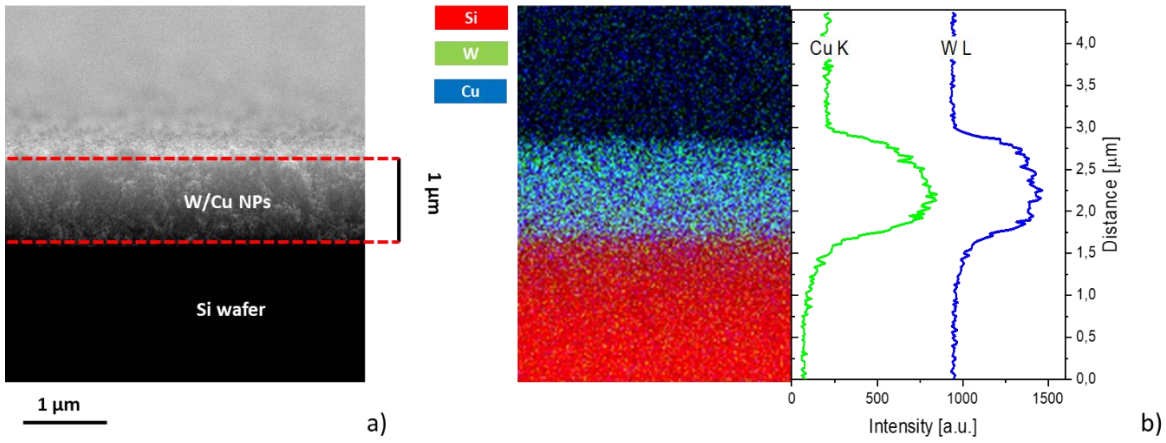

Figure 3 a) SEM image of the cross-section of W/Cu NPs film b) EDX map of Si, W and Cu (false colors) and corresponding depth profile of Cu and W. Offset is used for the elemental depth profiles

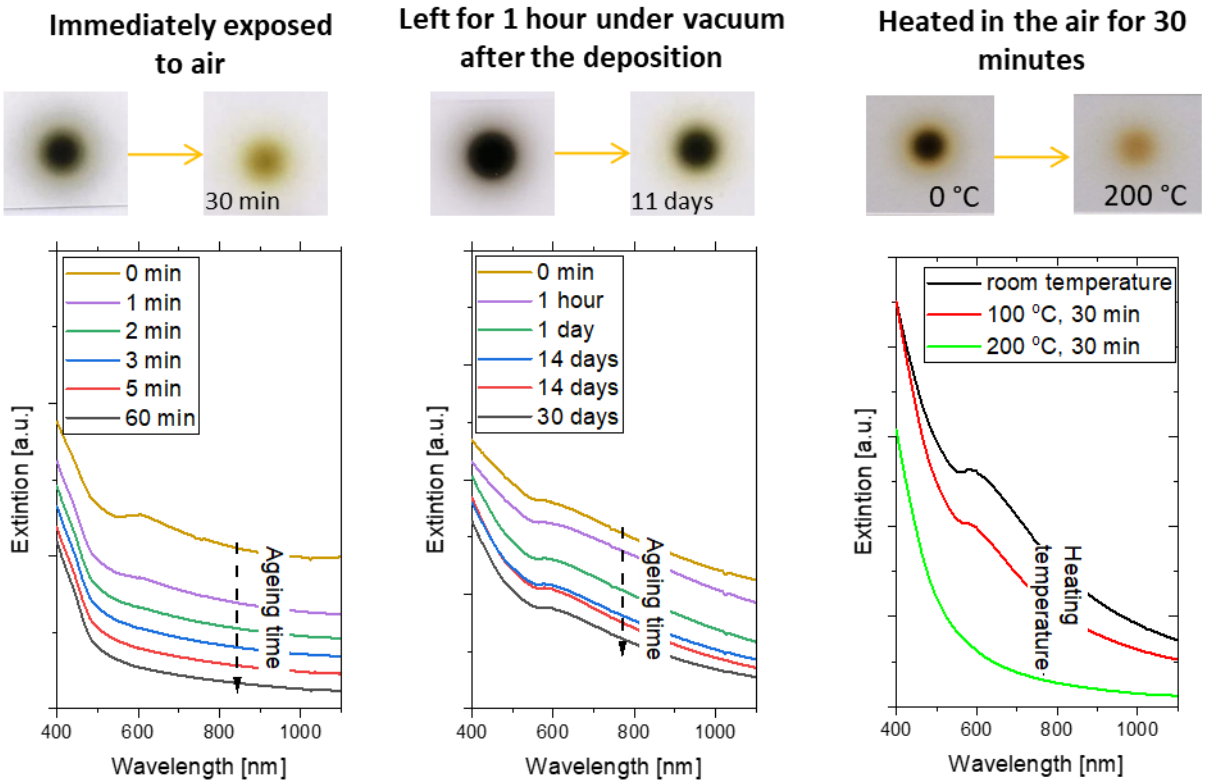

Figure 4 Variations in the UV-Vis spectra of W/Cu NPs with time when the samples were immediately after the deposition exposed to air a) or stored after the deposition of 1 hour under the high-vacuum b). c) UV-Vis spectra of W/Cu NPs films at room temperature and after the annealing at 100 °C and 200 °C for 30 minutes. For better clarity, the offset in UV-Vis spectra was used

UV-Vis measurements were used to describe the spectral characteristics of the deposited film (**Figure 4**). It was found that the localized surface plasmon resonance peak (LSPR) with maxima at about 610 nm that corresponds to Cu is clearly visible in the UV-Vis spectra. However, the LSPR peak readily vanishes with the time the samples spend in the open air and the sample changes its color from black to yellowish (**Figure 4a**).

This situation substantially changed when the W/Cu NPs films were after the deposition left under the high vacuum in the deposition chamber for 1 hour (**Figure 4b**). In this case, the color and LSPR peak stayed unchanged for a much longer time. In fact, the LSPR peak of Cu remained detectable even after one month. The possible explanation for such different behavior can be linked to the gradual oxidation of the samples. The oxidation of metals is promoted by an increased temperature. As shown in our previous studies with vanadium NPs [18], the NPs leaving the aggregation chamber may have a relatively high temperature exceeding 200 °C. When such NPs are immediately after the deposition exposed to open air, they are prone to oxidize. This effect can be limited when they are allowed to cool down without contact with air. To test this hypothesis, i.e., an important role of temperature on the oxidation of W/Cu NPs, the W/Cu NPs previously stored in high-vacuum conditions and aged in air for 1 month were heated to 100 °C and 200 °C for 30 minutes. As can be seen in **Figure 4c**, the copper LSPR peak was still well-visible for an annealing temperature of 100 °C, but it is completely suppressed when the annealing temperature was raised to 200 °C.

The last step of this study was the evaluation of the antibacterial activity of produced W/Cu NPs. In these experiments, PP meshes were used as a substrate. It was found that after 4 hours of incubation of the samples in the bacteria-containing media, almost a 2-log reduction of viable *E. Coli* bacteria was observed as compared to the number of bacteria incubated without W/Cu. This high antibacterial effect is predominantly connected with the release of copper ions from the samples exposed to aqueous media that reached after 4 hours level of 4.3±06 mg/L, i.e., a value comparable with the one measured on the purely Cu NPs film having the same thickness (6.2±0.4 mg/L).

4. CONCLUSION

It was demonstrated that bi-metallic W/Cu NPs can be effectively produced using a magnetron-based gas aggregation source with a segmental target. As shown, the deposition rate, in terms of the thickness of deposited NPs films, is as high as 100 nm/min and the synthetized W/Cu NPs have a core-shell structure with a tungsten core and approximately 2.5 nm thick continuous copper shell. Furthermore, it was found that the W/Cu NPs are prone to rapidly oxidize in open air. This effect may be to some extent slowed down if the NPs are allowed to cool down under high-vacuum conditions. Finally, it was proven that W/Cu NPs exhibit high antibacterial activity due to the release of copper ions.

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