PRODUCTION OF HETEROGENEOUS COPPER-TUNGSTEN PARTICLES

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Abstract

Gas aggregation cluster sources (GAS) represent one of the most rapidly developing systems for synthesis of nanoparticles (NPs). Such sources were used for the production of NPs from different materials ranging from metals or metal oxides to organic compounds. In recent years, the focus shifts to the production of heterogeneous NPs. In this work, we have studied the production of bimetallic NPs from copper and tungsten.

Keywords: Gas aggregation source, core-shell nanoparticles, copper-tungsten

1. INTRODUCTION

Metal nanoparticles (NPs) produced by means of gas aggregation cluster sources (GAS) represent ever growing field in nanoscience [1-5]. In the past, attention was paid to the construction of the GASes themselves [6,9], to understanding of the basic principles of the nanoparticle formation [1,2,12,15], the properties of single-phase particles and their transport to substrates [7,10,13]. The recent developments shift the focus from single material to composite nanoparticles. Simultaneous sputtering of two or more metals from several magnetrons in one aggregation chamber [8] allows for the production of multi-component NPs. However, good control over the component ratio is not straightforward in this case. The same problem arises when a single magnetron is used with a composite target which is split in two parts consisting of two different metals [11,14]. Other methods employ multiple steps such as in-flight coating of single-metal NPs by a thin film of another material [16]. It is possible to produce core-shell structure this way, but the method is rather complicated and usually produces only very thin shell. To prevent the above mentioned problems and keep the system as much simple as possible, we have decided to use a target with small pellets of other material set in the erosion track.

2. EXPERIMENTAL

The sputtering took place in a GAS based on a water cooled 3 inch magnetron with water cooled aggregation chamber walls (see **Figure 1**) in argon atmosphere at pressure of 60 Pa and magnetron current of 500 mA. The aggregation chamber was ended with a conical orifice of 2 mm in diameter. The GAS was mounted onto another vacuum chamber where the substrates for the depositions were placed. The distance between the orifice and the substrates was 10 cm. Pumping was performed by turbomolecular and scroll pumps.

The magnetron was powered with a DC generator (MDX 500) and set with three types of target: copper, tungsten and composite copper/tungsten. The composite target was designed in the form of a copper disk with tungsten pellets uniformly inserted along the erosion track. The pellets were of cylindrical shape 3 mm in diameter, the diameter of the erosion zone was 41 mm. The number of the W pellets determined the areal ratio between the two metals to be sputtered.

The NPs were characterised by scanning electron microscopy (SEM, Mira III, Tescan), X-Ray photoelectron spectroscopy (XPS, Phoibos 100, Specs) and survey Energy-dispersive X-ray spectroscopy (EDX, Mira III, Tescan). The deposition rate was monitored in-situ by quartz crystal microbalance (QCM) and the plasma was characterised by optical emission spectroscopy (OES, AvaSpec-3648, Avantes).

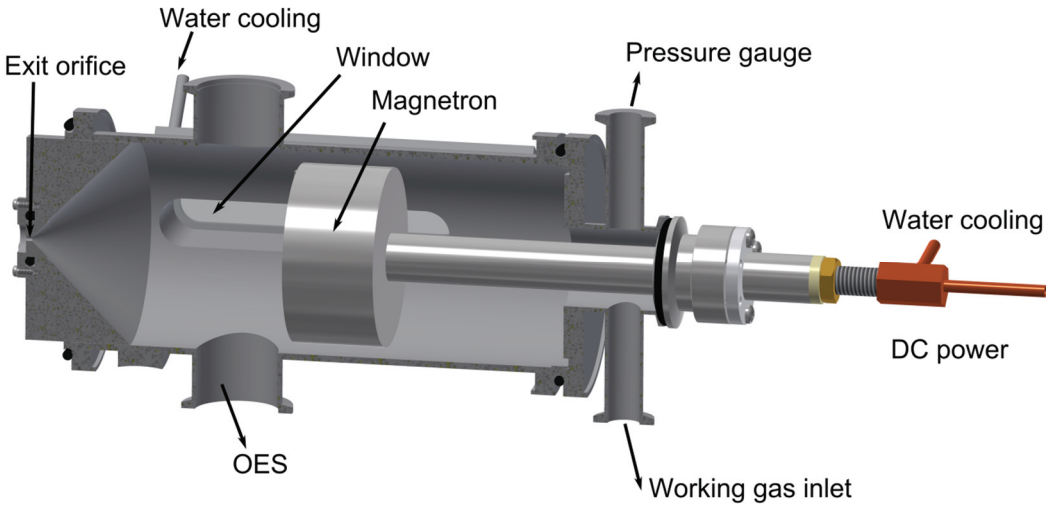

Figure 1 Schematic of the GAS

3. RESULTS AND DISCUSSION

The OES spectra of the discharge with different targets are shown in **Figure 2**. The spectra of the discharge with the single-metal targets show the lines typical for copper or tungsten, respectively. The spectrum of the discharge with the composite target shows the lines of both metals. Thus, OES appears promising for the in situ diagnostics of the bimetallic sputtering.

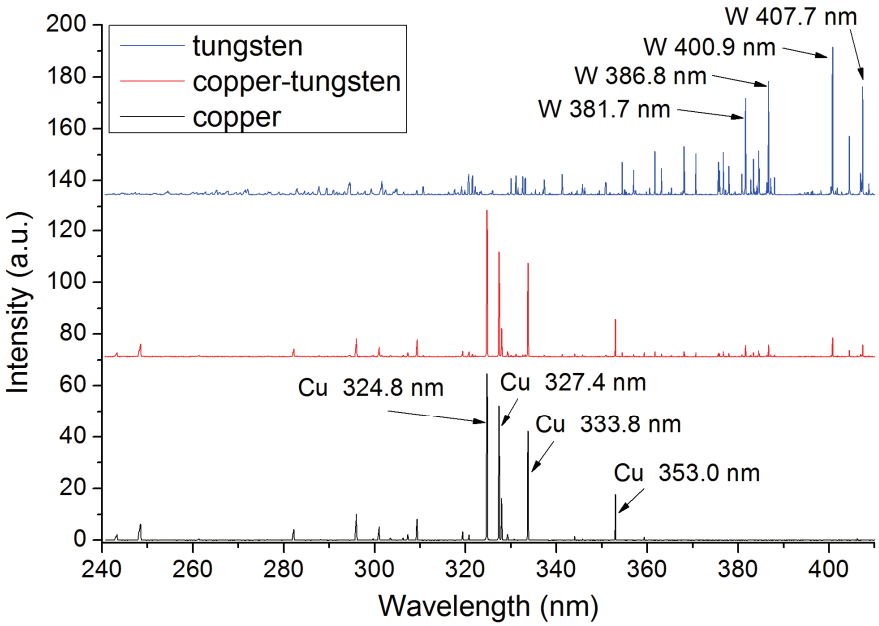

Figure 2 OES spectra of the discharge with three different targets

The SEM micrographs presented in **Figure 3** show that NPs are produced in all three cases. Single-copper sputtering results in the deposition of 43 nm-sized NPs whereas sputtering from the single-tungsten or from

the composite Cu-W target produces smaller NPs with the mean size of 16 nm. The addition of the tungsten evidently has a huge impact on the particle formation process.

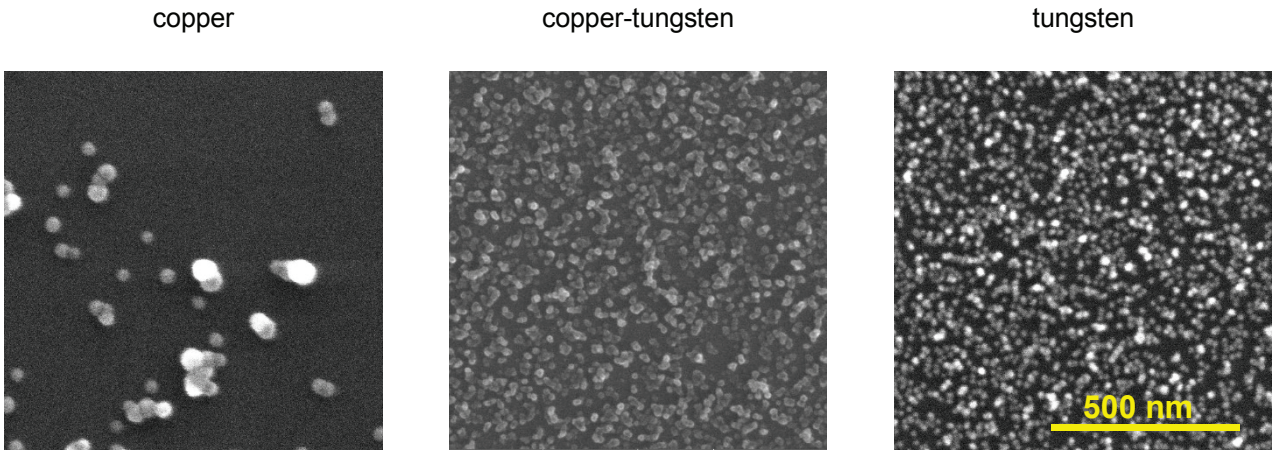

Figure 3 SEM images of the copper, copper-tungsten (39% of W in the composite target) and tungsten particles

The XPS and the EDX analyses were performed on the bimetallic Cu-W NPs shown in **Figure 3**. The XPS detected only 2% of tungsten and 98% of copper while the EDX revealed 15% of tungsten and 85% of copper. Different depth of analysis of the two methods provides the indication that Cu and W are not mixed homogeneously within the NPs but the outermost layers are enriched with copper.

HR-TEM analysis was performed on the bimetallic NPs to obtain deeper insight into their structural peculiarities. The NPs were produced with a higher amount of W pellets installed in the composite target to increase the areal percentage of tungsten to 91% and, hence, to stimulate the retention of tungsten in the final product. Indeed, the EDX measurements detected 40% of W in these NPs. **Figure 4** shows an example of the NPs produced in this manner. Obviously, the nucleation and growth of bimetallic Cu-W NPs proceed with the phase separation which leads to the development of a heterogeneous structure. Core-shell architecture of the NPs can be readily identified in which a 7 nm-sized W core is enveloped by a 2 nm-thick Cu shell.

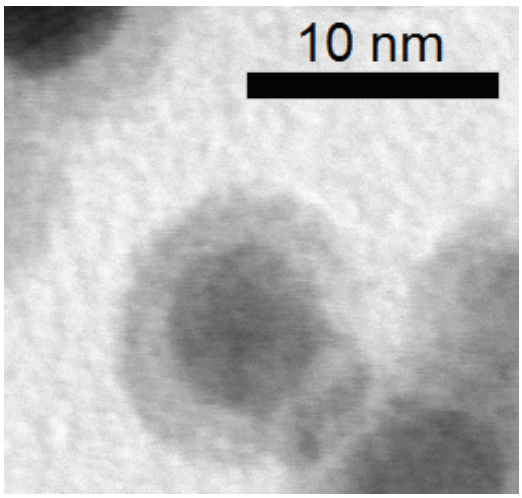

Figure 4 HR-TEM image of a particle containing 40% of tungsten

The presented method is foreseen to allow for the production of core-shell NPs with tuneable amount of the components. Special care should be taken though to regulate precisely the external parameters of the

discharge. For example, **Table 1** shows the magnetron voltage and the deposition rate measured during the sputtering. For the sputtering from the bimetallic target, the magnetron voltage remains markedly close to the value of the single-copper sputtering. However, for an unknown reason which is yet to be discovered, the deposition rate drops down to a value which is even lower than that of single-tungsten sputtering. Careful optimization of the sputtering is therefore inevitable. It should be also combined with the accurate investigation into physical processes occurring both on the surface of the target and in the gas phase to obtain deeper comprehension of the resultant NPs.

Table 1 The magnetron voltage and the NPs deposition rate

	copper	copper-tungsten (39% of W in the composite target)	tungsten
Voltage (V)	291	281	200
Deposition rate (Hz/s)	3.63	1.70	1.98

4. CONCLUSIONS

Core-shell nanoparticles of copper and tungsten have been successfully prepared using a gas aggregation cluster source from a composite copper-tungsten target. The composite nanoparticles have been compared to nanoparticles deposited from single metals, either copper or tungsten. The addition of tungsten to copper causes the composite nanoparticles to be much smaller as compared to the copper nanoparticles and to be of almost the same size as compared to the tungsten nanoparticles. The deposition rate of the composite nanoparticles drops below the level of copper or tungsten nanoparticles and needs to be carefully optimized.

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