Thin Solid Films 518 (2009) 1484–1488

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Synthesis and characterization of silver–carbon nanoparticles produced by high-current pulsed arc

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ARTICLE INFO

Available online 2 October 2009

Keywords:
Arc evaporation
High current
Silver nanoparticles
Surface plasmon resonance

ABSTRACT

In this paper, we report the formation of silver–carbon encapsulated metal nanoparticles (EMN's) using a high-current pulsed arc system in an argon atmosphere. The deposits were studied by Optical Extinction Spectroscopy (OES), X-ray diffraction (XRD) and Transmission Electron Microscopy (TEM); the chemical analysis of the deposits was performed using Energy Dispersion X-ray spectroscopy (EDX). Using the total nanoparticle diameter, the bulk crystalline density of silver and an estimate amorphous carbon (a-C) density we have calculated the size of the silver nucleus and the thickness of the a-C coating as a function of the argon gas pressure. The OES spectra of the EMN's exhibited two peaks characteristic of the Surface Plasmon Resonance (SPR) of elongated/very close silver nanoparticles; a subsequent thermal annealing strongly increased the SPR peaks. The double peak SPR spectra were modeled using calculations based on the existence of silver nanoparticles in the form of prolate spheroids. The main advantage of our preparation method is that the metal nanoparticles are encapsulated in a-C from the beginning and this layer acts as an efficient chemical barrier.

1. Introduction

The discovery of the formation of diverse nanostructured forms of carbon by the Kratschmer-Huffman carbon arc method and the modifications developed by Dravid have together generated a strong interest in the production of nanostructured materials for many applications. Such techniques have been used to produce not only carbonaceous materials but also a wide range of encapsulated metal nanoparticles (EMN's) using DC continuous arcs, of around 100 A in He, Ar or H at 26.7–66.5 kPa. However, there are a few reports of the advantages of using pulsed arcs in the same current range but the formation process of the clusters and nanoparticles is not fully understood. The interest in core–shell nanostructured materials arises from the fact that their intrinsic properties can be easily tuned by changing either their relative size [1] or the composition of both core and shell [2]. For example, both nanoshells (a dielectric core surrounded by a metallic shell) and nanocables (nanowires encapsuled in various kind of nanotubes) have been widely investigated recently [3–6].

One of the more interesting of such core–shell systems is composed of Ag nanoparticles encapsulated by crystalline or amorphous carbon. Silver exhibits outstanding optical properties and excellent thermal and electrical conductivity and therefore has been extensively used in catalysis, electronics, photonics, photography, biological labeling, surface-enhanced Raman scattering and optical devices [7–10]. However, these nanoparticles readily oxidize in air and have a poor biocompatibility; nevertheless, if a carbon shell is added both problems are solved and the range of prospective applications is increased. Based on this strategy, composite nanostructures using nanoscale silver as the core and carbon as the shell have been prepared by some groups. For example, Ag/C nanocables and Ag/C nanoparticles have been synthesized in the presence of PVP [11] and silver/cross-linked poly (vinyl alcohol) coaxial nanocables have been prepared [12].

In this work we have used High-current Pulsed electric arcs in Argon ambient between graphite (3.3×10^{-3} m of diameter) and silver (1.5×10^{-3} m of diameter) electrodes to produce silver–carbon nanoparticles. The resulting nanoparticles were analyzed by Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), Optical Extinction Spectroscopy (OES) and X-Ray Diffraction (XRD). The composition of the thin films was analyzed using energy dispersive X-ray spectroscopy (EDS) in a Cambridge-Leica, Mod. Stereoscan 440 Scanning Electron Microscopy, with an OXFORD Pentafet EDS detector.

There are various modeling approaches for the analysis of the OES data. In a previous study we have found that the T-Matrix method outlined below gives satisfactory results [13].

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doi:10.1016/j.tsf.2009.09.090

2. T-Matrix method

The T-Matrix method was originally developed by Waterman [14] and later improved by Mishchenko et al. [15–17]. The general idea of this method is to expand the incident and scattered fields, $\vec{E}_{inc}$ and $\vec{E}_{sca}$, in terms of appropriate sets of vector spherical harmonics $\vec{M}_{mn}$, $\vec{N}_{mn}$ [18]:

$$\vec{E}_{inc}(k\vec{r}) = E_0 \sum_{n=1}^{\infty} \sum_{m=-n}^{n} Rg[a_{mn}\vec{M}_{mn}(k\vec{r}) + b_{mn}\vec{N}_{mn}(k\vec{r})] \quad (1)$$

$$\vec{E}_{sca}(k\vec{r}) = E_0 \sum_{n=1}^{\infty} \sum_{m=-n}^{n} [p_{mn}\vec{M}_{mn}(k\vec{r}) + q_{mn}\vec{N}_{mn}(k\vec{r})], \quad (2)$$

where E_0 is the amplitude of the incident field, Rg is a normalization constant, a_{mn} and b_{mn} are the expansion coefficients, which are assumed to be known, and for an incident plane wave, are expressed in terms of associated Legendre functions and their derivatives [14] where p_{mn} and q_{mn} are the expansion coefficients characterizing the scattered field. These are obtained by multiplying the known expansion coefficients of the incident field by means of a so-called transition matrix or T-matrix:

$$\begin{bmatrix} p_{mn} \\ q_{mn} \end{bmatrix} = [T-matrix] \begin{bmatrix} a_{mn} \\ b_{mn} \end{bmatrix} = \begin{bmatrix} T^{11} & T^{12} \\ T^{21} & T^{22} \end{bmatrix} \begin{bmatrix} a_{mn} \\ b_{mn} \end{bmatrix}. \quad (3)$$

The T-matrix elements depend on the particle's size, shape, composition and orientation, but not on the nature of the incident or scattered fields. Now, expressions can be found to calculate the extinction and scattering cross sections from the T-matrix elements [18]:

$$\sigma_{ext} = \frac{2\pi}{k^2} \mathrm{Re}\left(\sum_{n=1}^{\infty} \sum_{m=-n}^{n} T^{11}_{mnm'} + T^{22}_{mnm'} \right) \quad (4)$$

$$\sigma_{sca} = \frac{2\pi}{k^2} \sum_{i,j=1}^{2} \sum_{n=1}^{\infty} \sum_{n'=1}^{\infty} \sum_{m=0}^{\min(n,n')} (2-\delta_{m0}) \left| T^{ij}_{mnn'} \right|^2. \quad (5)$$

Finally, before comparing the experimental results and the simulations, it is necessary to compute the optical density. The procedure is relatively straightforward and will not be described here; a detailed discussion has been offered, for example, in Ref. [19].

3. Experiment

The experimental apparatus is described in detail elsewhere [20,21]. For the metal carbon work, 3.12×10^{-3} m diameter high purity AERO graphite from ESPI and 1.5×10^{-3} m of diameter silver wire (99.9% purity) were used as the electrodes. The maximum arc current and its temporal form were sensed by measuring the voltage drop across a low inductance 0.98 mW resistor in the arc circuit, connected to a HP54522A Digital oscilloscope. The arc was generated in argon (99.99% purity) at pressures of 13 to 106 kPa and a 0.40 m diameter piece of glass tubing surrounding the electrodes was used to collect the deposit. For the TEM analysis, the deposit was removed from the inside of the tube by agitation in methanol using an ultrasonic bath. Drops of this liquid were then applied to a TEM grid coated with a holey polymer layer or for the SEM analysis the liquid was applied to a piece of high purity n type silicon wafer. The deposits were also characterised by X-ray diffraction, SEM and EDX. The composition of the samples was measured in an area of at least 5 μm^2.

Optical extinction spectra were obtained at room temperature using a Cary 500 double-beam spectrophotometer in the 330–800 nm wavelength range, before and after the thermal annealing, in order to detect the existence of the Surface Plasmon Resonance, indicative of the presence of silver nanoparticles. For these measurements the nanoparticles were deposited on a soda lime substrate and a thermal treatment was applied at 400 °C for one hour in an Argon atmosphere. The experimental OES spectra were compared with calculations of the optical density performed using the T-Matrix method [22], in order to find the parameters which provided the best fit. The bulk dielectric function values reported by Johnson and Christy [23] were used for the calculations, after applying a correction to incorporate surface dispersion effects [1].

4. Results

Fig. 1 shows that the maximum arc current linearly decreased as the argon gas pressure was increased from 13 to 106 kPa. The insert in Fig. 1 shows the temporal variation of the arc current; the FWHM duration of the arc is approximately 25 ms. Similar results of both the temporal variation of the arc current and the maximum arc current versus gas pressure, although with large values were observed using helium. Fig. 2a is a TEM micrograph of a nanoparticle prepared using an argon pressure of 40 kPa the crystalline silver nucleus and amorphous carbon coat can be clearly seen. More than 20 different sized nanoparticles were studied by tem and the carbon layer was always amorphous. The a-C layer was seen to be a very effective chemical barrier since no reaction was detected when nanoparticles were added to concentrated hydrochloric acid.

The left-hand side axis of Fig. 3 shows the average particle radius of the deposits prepared at the different pressures. This average radius was obtained from the measurements of at least 40 particles in SEM micrographs of the deposits. The average composition of the samples was measured over an area which included the 40 nanoparticles, only Ag, C, Si and O were detected (measurement of the silicon substrate without nanoparticles showed that the oxygen signal was from the native SiOx layer). Fig. 2b is a SEM micrograph of silver nanoparticles prepared at an argon pressure of 66 kPa, even though the micrograph shows less than the 50 nanoparticless referred to the selection gives a good idea of the distribution of sizes. Our earlier work [21] and the TEM analysis of the present deposits demonstrated that the nanoparticles consist of a small crystalline metal nucleus cover by an amorphous carbon layer. If we assume that the particle is spherical then:

$$\frac{m_C}{m_{Ag}} = \frac{\rho_C}{\rho_{Ag}} * \frac{r_{np}^3 - r_{Ag}^3}{r_{Ag}^3} \quad (6)$$

where m_C and m_{Ag} are the mass of carbon and silver in the nanoparticle, ρ_C and ρ_{Ag} are the densities of carbon and silver, r_{np} and r_{Ag} are the radii of the nanoparticle and the silver nucleus. This can be rearranged to give:

$$r_{Ag} = \frac{r_{np}}{\sqrt[3]{\frac{m_C}{m_{Ag}} * \frac{\rho_{Ag}}{\rho_C} + 1}}. \quad (7)$$

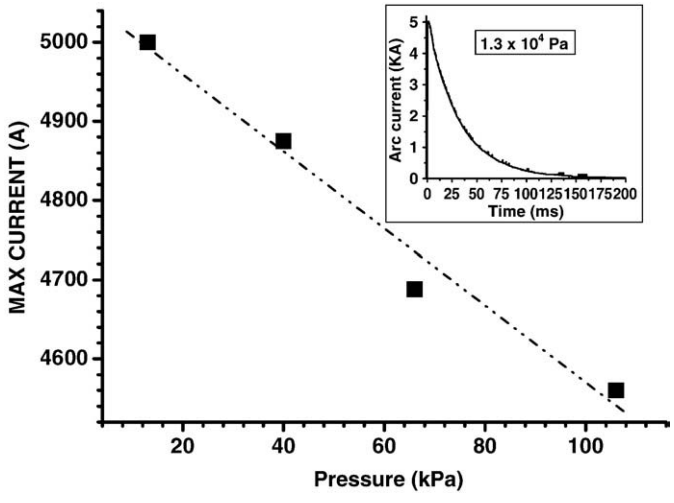

Fig. 1. The measured maximum of the arc current as a function of the argon gas pressure. The insert shows the temporal variation of the arc current for a gas pressure of 13 kPa.