Chemical Physics Letters 610–611 (2014) 363–368

Contents lists available at ScienceDirect

Chemical Physics Letters

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

Controlled formation of porous silver nanowires

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ARTICLE INFO

Article history:
Received 27 April 2014
In final form 24 July 2014
Available online 1 August 2014

ABSTRACT

Unusually long and highly porous silver nanowires (Ag NWs) are prepared via a simple but novel thermal evaporation process with substrate placed below the heated filament. Ag NWs growth processes are carefully monitored with respect to the time of vapour deposition keeping the filament-substrate distance fixed at 2 cm. As-prepared Ag NWs are analyzed by transmission electron microscopy (TEM), X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), optical absorption and surface enhanced Raman scattering (SERS). The present method for porous Ag NWs preparation has realized perhaps one of the best building blocks applicable to plasmonic waveguiding, nanophotonics and electrochemistry.

1. Introduction

Silver or generally noble metal nanowires have attracted extensive interest in recent years because of their unusual quantum properties and potential use as nano connectors and nanoscale devices [1–3]. To possess enhanced physical properties, the wires need to be of controlled diameter, high aspect ratio, and uniform orientation [2]. Nanostructured noble metal (Ag, Au, and Cu) thin film materials have stimulated extensive researches due to their unique physical properties their potential applications in chemical, biological analysis [4–6] and nanodevices [7,8]. Ag NWs have been attracting more and more attention because of the better electrical (6.3×10^7 S/m) and thermal conductivities ($429\,W\,m^{-1}\,K^{-1}$) among all kinds of metals and it has been extensively exploited many application areas including catalysis, electronics, photonics and photography, surface enhanced Raman spectroscopy [9,10]. Many research groups have focused their attention on the development of new nanostructures. Ag NWs and nanotubes, as one-dimensional (1D) nanostructures, have been extensively studied on their optical properties [11,12] as well as their potential use as conductive fillers to enhance the performance of the adhesives [13]. Although some progresses has been made in these research areas further investigations are still needed for better understanding and control the structure and morphology for application in devices, faster communication. Further uses of the Ag NWs could potentially enhance the SERS of molecules on the Ag nanowires decorated with individual metal nanoparticles which can be remotely excited by coupling external photons into the ends of the nanowires [14,15]. These Ag nanostructures exhibit a wealth of optical phenomena directly related to their geometry-dependent surface plasmon resonances (SPR), which provide the basis for the construction of Ag-based biosensors [16,17] and help to understand SERS [18,19]. SERS substrates are expected to be anisotropic in terms of the SPR in metallic nanostructures. If probe molecules are located in such nano pores as local Raman "hot spots" the Raman scattering can be strongly enhanced due to local electromagnetic field enhancements. Recent investigations have further extended into the plasmon propagation along thin Ag NWs as highly promising plasmonic waveguides in photonic and electronic devices [20,21]. Plasmon coupling phenomenon for nanowires system has also been extensively investigated both theoretically and experimentally. Up to now, several methods for the synthesis of Ag nanowires have been developed. These methods include chemical synthesis [22], electrochemical technique [23] hydrothermal method [24] DNA template [25,26] and porous materials template [27] assisted synthesis and polyol process [28,29]. Among all these chemical methods, cost-, yield-, and simplicity-wise, the physical vapor deposition process seems to be the most promising one. In this wide scenario high purity with controlled nano wire diameter with porous structure having low cost procedure with high reproducibility represents an appealing goal, because Ag NWs are potentially useful materials in the field of quantum optics. As there is much to learn about the properties of nanowires and other nanoscale structures to build a useful knowledge base leading to numerous applications development of new method of nanowire synthesis is timely and mandatory.

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http://dx.doi.org/10.1016/j.cplett.2014.07.056
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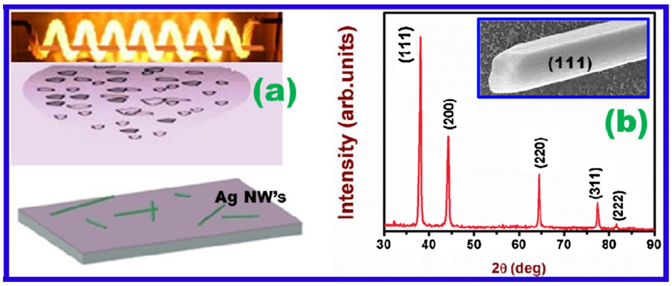

Figure 1. (a) Schematic view of Ag porous nanowire formation (b) X-ray diffraction patter of Ag nanowire.

The above discussion shows that the novel one dimensional (1D) nano structures are difficult to be synthesized via other chemical methods and there is an urgent need to develop simple innovative alternative. In this article, we report a convenient and inexpensive way to produce a high yield/high porous with controlled size dependence of Ag NWs well established and widely used for large-scale production. The physical vapor deposited Ag NWs is shown to drastically enhance surface plasmon propagation distances and are thus believed to be promising candidates for applications such as interconnects in integrated optical and electronic circuits at nanoscale due to advantages such as high crystallinity and nanoporous surfaces.

2. Preparation of Ag nanowires

Ag NWs were prepared by using thermal evaporation (or physical vapor deposition) method (HIND HIVAC VACCUM COATING UNIT model: 12A4) the precursor being highly pure Ag wire (Aldrich 99.99%). Ag thin film deposition was carried out under good vacuum conditions at 4.3×10^{-6} Pa. Figure 1(a) represents the schematic diagram of Ag NWs prepared under heated filament with 2 cm target to substrate distance. The heating filament method essentially works on the Joule effect principle [30,31]. The heated silver vapors were evaporated from the filament and deposited on the bottom substrates maintaining constant power (30 V) during the deposition time. The pure Ag NWs were prepared with controlled time of deposition and heated filament to substrate distance maintained as 2 cm. It is important to note that the heat/temperature distributions around the heated spiral are quite different for the 'substrate – above – filament' and substrate – below – filament configuration. This is the crux of the present novel and general method of nanowire fabrication, applied here for making unusually long Ag nanowires.

2.1.1. Characterization

Ag NWs were structurally characterized from X-ray diffraction (XRD) pattern, which was recorded by using a BRUKER X-ray diffractometer equipped with Cu Kα radiation (Cu Kα λ = 1.5406 Å) in the 2θ range of 30°–90°. Optical absorption spectra of nanostructured thin films were scanned using a UV–vis Spectrophotometer (JASCO model no 7800) in the wavelength range 300–800 nm. The morphology of the samples was analyzed using a Field emission scanning electron microscope (FESEM ULTRA-55) equipped with an energy dispersive spectrometer (EDS) and transmission electron microscopy.

2.2. Preparation for SERS measurements

Rhodamine 6G (R6G) dye is used as the Raman probe for the SERS measurements. For SERS substrates preparation, R6G is dissolved in ethanol and produced R6G solution. The as prepared silver thin films were immersed in R6G solution and the films was thoroughly dried in air. Raman spectra of Ag films were recorded by a micro-Raman spectrometer (LABRAM-HR) using laser excitation source of 514.5 nm (Ar^+).

2.3. Growth Mechanism of Ag NWs

The Ag NWs are formed in the vacuum chamber under the heated filament with a 2 cm distance from target to substrate. It appears that the average temperature at the substrate could provide enough energy required for the activation of specific faces for the anisotropic growth of 1-D nanowires with high porosity. Both the dissolution of small silver nano particles and the diffusion of heated-silver atoms on the substrate have resulted in the formation of silver nanorods or Ag NWs. Realizing high temperatures seems to favor the formation of highly porous Ag NWs shown in Figure 1(a). By carefully analyzing the XRD/TEM/FESEM as prepared Ag thin films of different thickness, it is found that the Ag NW's had an average diameter ranging from 150 to 450 nm shown in Figure 5. Ag NWs are very likely formed through an adhesion process followed by subsequent heat diffusion under the present vacuum conditions. Figure 4(a–d) shows the FESEM images which strongly indicate that Ag NW could nucleate and grow on the pre-formed 1-D nanowires.

3. Results and Discussion

3.1. XRD

Figure 1(b) shows the XRD patterns of the Ag nanowires. The diffraction peak 2θ values at 38.08, 44.31, 64.44, 77.37, 81.57 of corresponding to the (1 1 1), (2 0 0), (2 2 0), (3 1 1), and (2 2 2) planes face centered cubic (fcc) silver [32]. The lattice constant calculated as 0.4083 nm, and the value are agree with the literature value (a = 0.4083 nm Joint Committee on the Powder Diffraction Standard card number 89-3722). Moreover, all diffraction peaks of the product show stronger peak intensities than usually observed for polycrystalline silver, indicating that the obtained Ag NWs possess high crystallinity with the (1 1 1) diffraction peak having the highest intensity. Compared with the standard pattern of fcc Ag, an intense (1 1 1) reflection peak was observed in the XRD pattern, indicating that the particles have preferential orientation along a specific (1 1 1) direction. The relative intensity in diffraction pattern are depends upon the crystal structure and the lattice orientation of crystallites. It is obvious that the intensity of peak at 38.08° and corresponding plane (1 1 1) is much stronger than the other peaks, which means that Ag NWs have preferred (1 1 1) orientation. Since (1 1 1) surface of fcc-structured metal nanoparticles has different the electronic structure from (2 0 0) and (2 2 0) surfaces, preferentially interacts chemically with certain crystallographic orientations of silver metal to stabilize silver nanostructures with anisotropic shape [33]. The strongest (111) peak may indicate the preferred orientation growth of fcc-Ag NWs along the [1 1 1] direction, which is also suggested by the TEM/FESEM. The XRD pattern indicates that the sample has no orientation effects, since the intensities agree fairly well with those reported for [34]. The observation of these reflections for the prepared Ag NWs sample indicates that the silver nanowires are obtained in a crystalline form without any further thermal treatment.

Figure 2 shows the TEM images of an Ag NWs with a diameter of ∼80–300 nm. Figure 2a shows the Ag NW with 80 nm diameter clearly showing the formation of Ag NW with high (111) orientation and good porosity (pore size ∼2–5 nm) shown in Figure 2b. In Figure 2c, 200 nm film Ag NWs having ∼300 nm diameter with high yield (check in supplementary information) and the selected area