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The study of silver nanoparticles by scanning electron microscopy, energy dispersive X-ray analysis and scanning tunnelling microscopy

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The authors present results of studies on commercially available silver nanoparticles fabricated by Amepox Microelectronics and delivered in the form of silver powder. The studies were carried out by scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX) and scanning tunnelling microscopy (STM). Chemical analysis performed with the use of EDX revealed that the powder contains about 74% of silver. Further studies of the silver granulate by use of SEM explicitly indicated the presence of micromete-size conglomerates composed of much smaller particles. Silver powder was dissolved in *n*-hexane, and colloid solution was obtained, in which the particles were subjected to the process of segregation. The colloid, obtained with this method, in which one expected to find particles of smaller sizes, was deposited on the Au(111) surface. The results of the studies of the sample prepared by means of STM enabled us to estimate the distribution of silver nanoparticles size, which appeared to be normal with a relatively small standard deviation.

Key words: *silver nanoparticle; STM; SEM; EDX*

1. Introduction

Over the past few years, studies on nanosilver have remained of interests to many scientific groups because of its potential technological application in many spheres of life. The properties of silver nanoparticles investigated so far allow their use among others in medicine [1, 2], optics [3, 4], or in electronics [5, 6]. From the nanotechnological point of view, the application of nanosilver in the form of colloidal ink for forming conducting tracks with micrometrical width [7, 8] is of potential interest.

The technique of producing silver particles of nanometrical size is well known and widely used. It is based on thermal decomposition of silver salt of a fatty acid in the atmosphere of neutral gas (Argon) [9]. As a result of that process, powder consisting of silver particles surrounded by stabilising substances in the form of alkyl chain is

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obtained. Such particles demonstrate strong tendency for aggregation and formation compact micrometrical structures [10] only possible to segregate in organic solvents such as toluene, hexane, benzene [11].

In this paper, we describe results of nanosilver studies carried out by means of the following techniques: scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX) and scanning tunnelling microscopy (STM). Studies carried out by SEM and EDX, global techniques, enabled not only a detailed examination of silver powder morphology, but also its chemical composition analysis. However, they appeared insufficient for distribution analysis of single particle sizes. For this purpose, the STM high resolution technique was used. In the conducted experiment we managed to separate particles from the silver powder by means of hexane and then deposit them on the Au(111) surface. It allowed us to observe single particles with the use of STM and carry out a detailed distribution analysis of their size. The results we obtained proved a narrow particle size distribution which is well described by normal distribution.

2. Experimental

We used nanosilver in the form of silver powder supplied by Amepox Microelectronics. The studies of silver powder were carried out by means of a scanning electron microscope Vega 5135 MM from Tescan company (SE Detector, 30 kV, high vacuum 5×10^{-3} Pa) working with EDX Link 300 ISIS from Oxford Instruments (Detector Si(Li), 30 kV, low vacuum 10 Pa, resolution 60 eV). The samples were prepared by fixing the powder particles to microscope holder, using a conducting carbon strip.

For single nanoparticle studies, we used a home-built STM [12] working in air at room temperature. Preparing the sample required separating single silver particles from the powder delivered for studies. For this purpose, we dissolved 1 mg of silver powder in 5 ml of hexane (Aldrich, Chromasolvz, 97%). The solution prepared in this way was subjected to the process of particles selection. Particles of sizes larger than nanometrical, deposited on the test tube bottom formed sediment but the smallest ones formed a homogeneous colloid solution. After 24 hours, 20 μl of the obtained colloid was additionally dissolved in 5 ml hexane, which allowed obtaining a transparent solution which was deposited on the Au(111) surface (Georg Albert PVD – Beschichtungen). After the evaporation of the solvent (two hours), the sample was examined with the STM microscopy. The studies were carried out under constant current mode I_t =1 nA, at tip sample voltage U_t = 0.2 V. For the experiment, we used a mechanically sharpened, platinum-iridium tip (Pt 90%, Ir 10%).

3. Results and discussion

Figure 1 shows typical results of the studies of silver powder deposited on a carbon strip by means of SEM. Part (a) of the figure represents the view of the sample at 300× magnification which stands for examining the area of 800×800 μm^2 surface. Around the examined area, one can notice the presence of objects of sizes within 200 μm to 300 μm. Those objects consist of tiny particles, as can be proved by SEM studies results gathered on one of the particles.

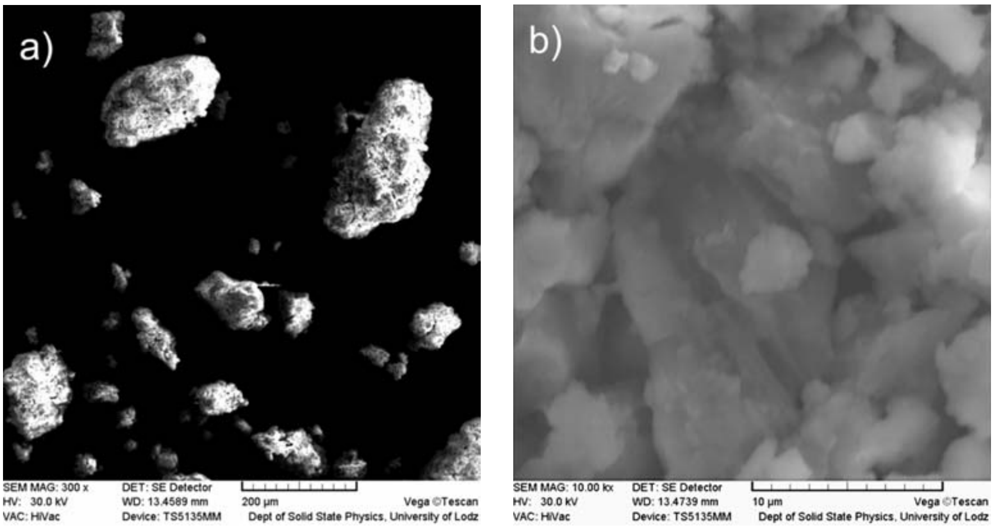

Fig. 1. SEM pictures of silver powder granulate deposited on a carbon strip:
a) 300× magnification, b) 10 000× magnification. An example of strong aggregation of particles in the granulate, lack of visible nanoparticles

The above results are shown in Fig. 1b (25×25 μm^2 area, magnification 10 000×). It is easy to notice that the examined particles consist of a number of smaller objects of 0.5 μm to few micrometers in size. However, we did not manage to examine the structure of the observed nanoparticles because of difficulties connected with getting higher magnification. The problem was caused by washing out the details on SEM picture which appeared as a result of sample charging. The charging evidences low electric conductivity of the medium. It should be mentioned that the examined silver nanoparticles are surrounded by a nonconducting carbon stabilizer. In our opinion, the stabilizer is responsible for sample loading effects during the attempts of receiving a higher magnification. Another factor responsible for difficulties connected with getting higher magnification was high susceptibility of nanoparticles to aggregate into larger conglomerates. We should point here that, except for nanoparticle conglomerates, in silver powder there may appear stable grain of size ranging even to single micrometers. It is not unlikely that a part of the examined objects belongs to such categories.

In Figure 2, a standard EDX spectrum recorded on the examined sample is shown. In the middle part of the presented spectrum one can clearly see five peaks located between 2 kV and 4 kV. Those maxima are directly related to the silver characteristic lines K and L. The maximum located on the left part of the spectrum at 0.2 kV clearly comes from carbon. The hardly visible maximum located at 0.5 keV is connected with the oxygen characteristic line. The carbon and oxygen spots in the examined samples confirm the presence of stabilizers composed of alkyl chains. The spectra obtained during EDX studies were used for carrying out the quantitative analysis. For that purpose, SEMQuant software and the ZAF procedure were applied. Quantitative analysis proved high silver contents (74%) in the examined samples. Except for silver, we also show the presence of coal and oxygen, the contents of which amounted to 21% and 5%, respectively.

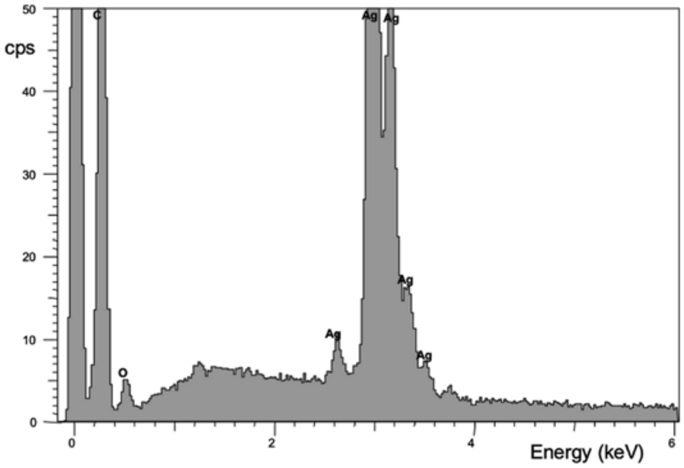

Fig. 2. EDX characteristic spectrum obtained for silver powder. Visible peaks confirm the presence of carbon and oxygen substances in the sample

Because of the failure of examining particles at high magnification with SEM, we decided to use microscope allowing picturing conducting surfaces with single nanometer resolution – STM. However, low conductivity of particles seemed to be an obstacle, which was indicated by SEM studies. But we should remember that STM can picture the areas and objects having relatively high resistances because of a high resistance of the tunnel junction. An additional argument for using STM was the relatively high silver contents in the examined samples, as well as their grained structure. In order to carry out STM studies, we had to use an additional preparing procedure by dissolving the powder in hexane.

The particles of nanometer size were separated and deposited on Au(111) surfaces, which was chosen as a surface for STM studies. In Figure 3a, a topographical 150×150 nm^2 STM picture of pure Au(111) just before deposition of particles is shown. In this picture, one can see large monoatomic flat area surfaces and a monoatomic 0.24 nm high step. Additionally, the height profile recorded along white arrow depicted in the figure is shown in the inset. Such topographic pictures are characteristic of pure gold and were recorded in various parts of Au(111) surfaces. After deposition of particles, we could also observe monoatomic flat terraces and 0.24 nm high steps. But we also notice additional objects, not observed on pure gold. A typical topographical picture, obtained after deposition is shown in Fig. 3b. One can see that although thiol was not used as substance for binding nanopartilces to the gold surface [3], we managed to deposit firmly the sample.

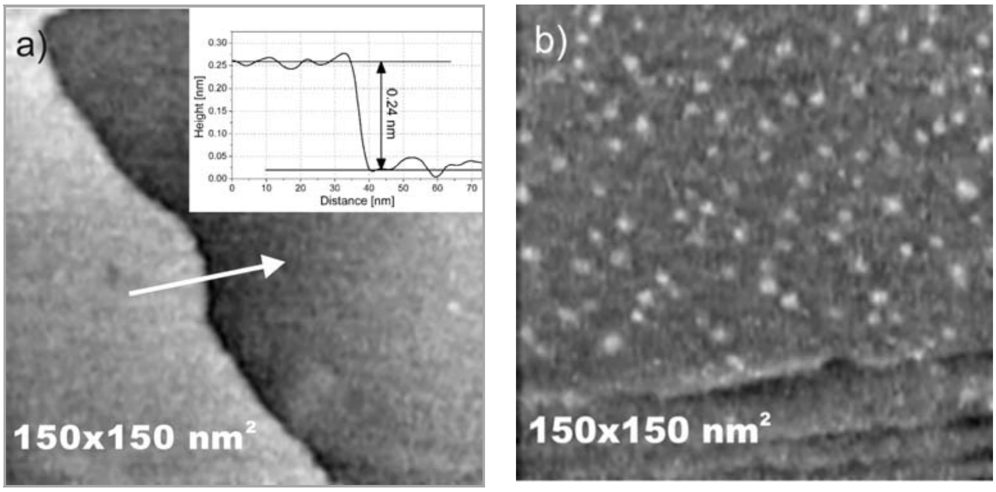

Fig. 3. The STM picture of Au(111) surface before (a) and (b) after silver nanoparticle deposition, the area of scanning –150×150 nm^2. Inset in Fig. 3a shows the height profile taken along an arrow depicted in the figure

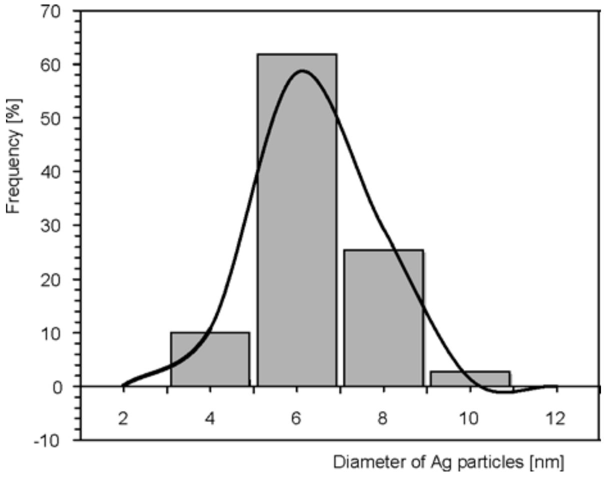

Fig. 4. The histogram of silver nanoparticles sizes obtained by means of the STM results

A sample prepared in this way exhibited stability during the studies in air and lack of coagulation processes. Observation of immobile single nanoparticles enabled the analyses of their size distributions. The obtained histogram (Fig. 4) confirms the fact that for 100 observed nanoparticles – distribution of their sizes is a narrow normal one with a 6.4 nm average value and a 1.4 nm standard deviation. The theoretical curve of standard distribution fitted to the results of our studies (Fig. 4) was calculated by means of MS Excel program. The nanoparticle sizes calculated by us are comparable with the results of similar studies conducted with other measurement techniques [14, 15].

4. Conclusions

The obtained results of SEM and EDX studies confirm the fact that silver powder consists of micrometrical conglomerates which contain large amounts of silver (about 74%). During the studies, we have managed to separate single nanoparticles from the powder and deposit them on Au(111) surface without using thiol molecules. The results of STM studies demonstrated that the colloid created specially for these studies contained nanometrical particles and the nanoparticle silver analysis has shown that spread of sizes is a subject of normal distribution with a 6.4 nm average value and a 1.4 nm standard deviation

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