

The applicability of global and surface sensitive techniques to characterization of silver nanoparticles for Ink-Jet printing technology

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1. Introduction

In recent years, silver nanoparticles (AgNPs) have been investigated by many research groups all over the world (Klabunde, 2001). It is mainly due to potential applications of this new nanomaterial in modern electronic devices (Xue et al., 2006), medicine (Shahverdi et al. 2007), optics (Mc Farland et al., 2003) and biology (Huang et al., 2004). Among others it is promising to use AgNPs in electronic industry to create printed circuits due to good electric and thermal conductivity of silver. This is commonly performed by the use of so called Ink-Jet printing technology.

Ink-Jet printing is based on throwing onto substrate picoliters portions of ink containing nanoparticles of metal (especially silver) which could be formed in micrometer dots and tracks (Fuller et al., 2002). In consequence it is possible to print any matrices consisting micrometer elements which after further treatment can be used as a electronic tracks and devices. This technology requires well defined and stable metal nanoparticles which remain on surface after evaporation of solvent which forms stable colloid (ink). Nanoparticles usually contain a metal (nanocrystalline) core and an outer shell - surfactants or ligands, which typically are alkyl (Jiang et al., 2002) or polymer chains (Tsuji et al., 2008). The presence of organic molecules stabilizes nanoparticles, prevents their aggregation and facilitates creation of colloid. Unfortunately, it is also responsible for insulating character of printed structures. To make them conducting thermal sintering process is required. It results in ligands decomposition and in the crystallization of silver cores (Smith et al., 2006).

We present our results related to physical and chemical characterization of ligand-stabilized silver nanoparticles (Amepox MC) using different experimental methods. Particularly, we focus on problems associated with estimation of size distribution of silver nanoparticles using: high resolution transmission electron microscopy (HRTEM), atomic force microscopy (AFM), dynamic light scattering (DLS) and ultraviolet and visible spectroscopy (UV-VIS) - the similarity and the differences between these techniques will be briefly outlined. The

global chemical analysis by using energodispersive X-ray spectroscopy (EDX), and the surface chemical analysis by using X-ray photoelectron spectroscopy (XPS) of AgNPs deposited on different substrates will be presented and the applicability of the used techniques described. Finally, the global ultraviolet photoelectron spectroscopy (UPS) and local scanning tunnelling spectroscopy STS techniques, will be presented as a valuable techniques in electronic structure investigations of AgNPs. This is especially important in the case of studies of quantum size effects on nanoparticles.

1.1 AgNPs for Ink-Jet printing

The most popular nanomaterials for Ink-Jet application are silver nanoparticles synthesized by thermal decomposition method (Khanna et. al., 2008). This method is based on decomposition of silver salt of fatty acid at high temperature in inert atmosphere (Fig. 1). Silver salt (silver alkanoate) is obtained as the result of the reaction of silver nitrate and fatty acid dissolved in sodium hydroxide water solution. The proportions of compounds are very important. For example using of: 52g of AgNO_3 , 75g of myristic acid, 12g of NaOH and 1L of high-purity water (Nagasawa et al., 2002) seems to form good proportions to prepare initial solution. The next step is a decomposition that received silver alkanoate in inert atmosphere. Such process could be realised in two ways. According to Nagasawa et. al. 2002, stable silver nanopartilcs with narrow size distribution could be obtained as a result of thermal decomposition of silver alkanoate in nitrogen atmosphere at 250°C . Recently Shim et. al. 2008, suggest reaction at 210°C in liquid solution – fatty acid dissolve in non-polar and slowly evaporating solvent (for example 1-octadecene). The both reaction give silver powder composed of strongly aggregated ligand-stabilized AgNPs with narrow size distribution. However, the efficiency of the reaction, the size of the final product and stabilization of nanoparticles in solvent strongly depend of annealing temperature.

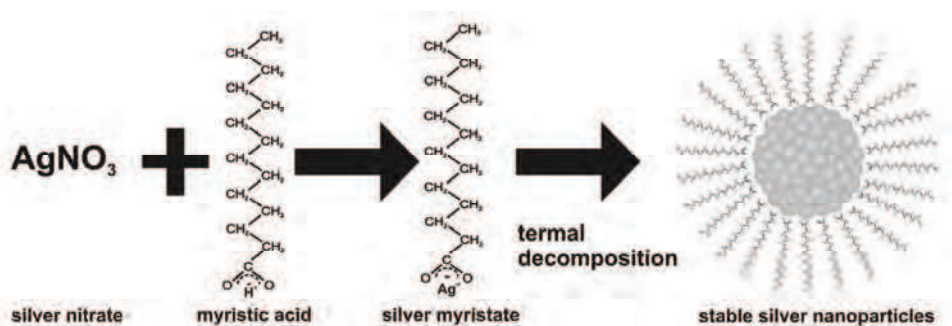


Fig. 1. Schematic of the thermal decomposition synthesis of the stable silver nanoparticles with fatty acid coated.

Preparation silver ink requires dissolving of the synthesised silver powder in non-polar organic solvent (usually *n*-tetradecane). Tracks printed using such ink become conductive after sintering at $240 - 250^\circ\text{C}$ for 30 min.

In our experiments we investigated commercially available silver powder synthesized using thermal decomposition method in Amepox Microelectronics laboratory (Moscicki et. al.,

2007). For characterisation we re-dissolve that material in cyclohexane (Aldrich) what give good quality colloid with low concentration of AgNPs.

2. AgNPs characterization

The quality of the ink and its properties depend mainly on size distribution and chemical composition of nanoparticles. There are many techniques which could be used to perform such measurement however among others a few are most popular and widely used:

- high resolution transmission electron microscopy (HRTEM);
- atomic force microscopy (AFM);
- dynamic light scattering (DLS);
- ultraviolet and visible spectroscopy (UV-VIS).

Each of these techniques are based on different physical property and because of that they return slightly different distributions. Two of them are global techniques which give information about average distribution in whole sample (DLS, UV-VIS). Other two are local which allow to measure shape and diameter of individual nanoparticles (HRTEM, AFM). Beside that some of them measurement is performed in solvent (DLS, UV-VIS) while other require earlier deposition of nanoparticles on the substrate (HRTEM, AFM) which could result in distortion of their diameter. Because of these properties more than one technique of diameter estimation should be used.

Beside of size distribution measurements chemical analysis of nanoparticles is often performed using mainly three techniques:

- X-ray photoelectron spectroscopy (XPS);
- energodispersive X-ray spectroscopy (EDX);

Due to different probing depth XPS could be qualified as a surface technique while EDX is rather bulk like. XPS and EDX could give information about chemical composition and XPS could be used to estimate type of bonds formed between surfactant and metallic core as well as in surfactant itself.

2.1 Size distribution measurement

The first technique which we used, was high resolution transmission electron microscopy (JEOL JEM2000EX HRTEM). Fig. 2(a) shows a typical electron micrograph recorded on silver nanoparticles. It is clearly seen that their spatial distribution is random which is a typical result in case of drop cast method. More controlled sample preparation and better spatial distribution of nanoparticles could be achieved using Langmuir-Blodgett (LB) which results in high quality monolayers of nanoparticles (Lu et. al., 2005). Despite the preparation method the estimation of AgNPs size distribution are similarly. By measuring of about 250 individual particles we were able to create a histogram which is shown in Fig. 2(b). It is clearly seen, that the obtained histogram is not really symmetrical due to a low amount of small AgNPs and almost constant number of counts in the range of 5 - 6 nm. Nevertheless, we decided to fit our experimental data with normal distribution. Fitted distribution (shown in Fig 2 (b)) is characterised by the mean value and standard deviation equal 5.5 nm and 1.5 nm respectively. This result is consistent with reports of other research groups (Abe et. al. 1998). It is worth noting again that HRTEM is only sensitive to silver cores (crystalline) size. The organic shell is not observed on electron micrographs, however distances between cores could be used to estimate ligands lengths.

Another microscopic technique which was used in our experiments was atomic force microscopy (home build (Klusek et. al., 1998)). Due to its local character and huge magnifications this technique found its application in nanoparticles investigations world wide. Especially AFM is used to estimate their diameter. Commonly tapping mode is used which is believed to be less interacting with NPs than contact mode. In our experiments we prepared samples in similar way like in case of HRTEM studies. Silver nanoparticles were deposited on atomically flat Muscovite (001) surfaces by drop cast method.

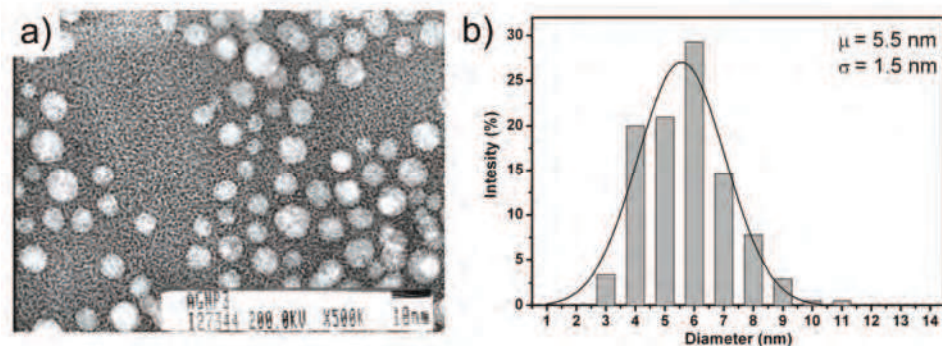


Fig. 2. The measurement of nanoparticles diameter by means of HRTEM: (a) electron micrograph, (b) estimated histogram.

In Fig. 3(a) we present the $1400 \times 1400 \text{ nm}^2$ AFM topography of AgNPs decorated the Muscovite (001) substrate. The image evidently shows the nanoparticles of different size dispersed randomly on the whole surface. Although, it is easy to observe the single isolated nanoparticles one can also notice that nanoparticles tend to form bigger structures, conglomerates as a result of coagulation process. The nanoparticles were not chemically bonded to the substrate, however, we found out that the sample was stable during investigation in the air which allowed us to measure size distribution of nanoparticles. In order to minimize the effect of AFM tip radius in the measurements, a height of the particles has been measured (Ebenstein et. al., 2002). In Fig. 3(b) we present a histogram of the particle height distribution. The mean value and the standard deviation are 4.3 nm and 1.2 nm, respectively.

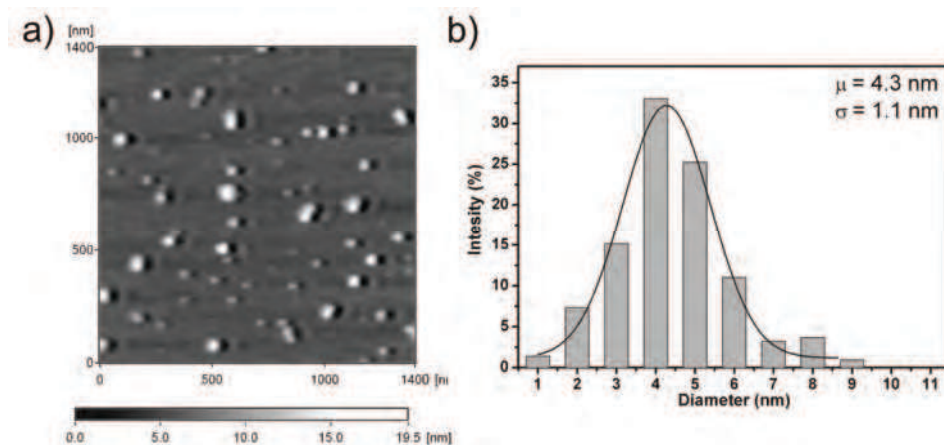


Fig. 3. AFM measurement of nanoparticles diameter: (a) topography image, (b) estimated histogram of high distribution.

This results which we recorded are different than these obtained using high resolution transmission electron microscopy. Because we expect that AFM should be sensitive not only to metallic cores like HRTEM is but also to ligands. Thus, we expected to obtain mean value at the level of 8 nm (5 nm silver core and 2×1.4 nm long alkyl chain). Much lower value could be related with specific properties of investigated system. In case of homogeneous samples, height measurement is quite precisions. However, nanoparticles are composed of 5 nm silver cores capped by 1.4 nm long alkyl chain which form highly not homogenous system. Such system could behave in various ways after depositing on substrate. At least three different behaviours are expected: (i) ligands forms spherical shell around core and AFM does not interacts strongly with the NPs, (ii) alkyl chains are distorted or even removed at the substrate core interface but interaction with the cantilever is weak and (iii) there is strong interaction with the substrate and also alkyl chains bend as a result of presence of the cantilever. Each of these situations would result in different apparent height starting from 8 nm and finishing on 5 nm. We think that in our case we dealt with situation (iii) which could explain height distribution which would reflect real core diameters. However situation is much more complicated because different values of height could be obtained after deposition of nanoparticles on different substrates. For that reason, AFM seems to be not a good technique to precisely estimate diameter of ligand-stabilized small nanoparticles or clusters (<2 nm) (Hornyak et. al. 1998). However, this effect can be ignored when diameter of nanoparticles are 20 nm or bigger.

In the next step, we used techniques based on optical properties of nanoparticles: UV-Vis (Hitachi U-1900) and DLS (Zetasizer 1000HS by Malvern Instruments). Ultraviolet and visible light spectrometer is an instrument mainly used to characterise the optical properties of materials, especially to estimate the surface plasmon resonance peak. It could be used to measure the mean value of nanoparticles core radius. It is possible using Gustav Mie theory of light scattering by spherical particle (Mishchenko et. al., 2002). This theory is described in terms of two parameters:

- normalized refractive index n_r ;

$$n_r = \frac{n_p}{n_m}, \quad (1)$$

where n_p is refractive index of particles and n_m of surrounding medium

- size parameter x :

$$x = \frac{2\pi r n_m}{\lambda}, \quad (2)$$

where r is particles radius and the light wavelength λ .

According to the Mie theory, efficiency of scattering is expressed by:

$$\sigma_s = C_s A, \quad (3)$$

where A is a geometrical area of particles and C_s - scattering coefficient.

The scattering (C_s) and extinction (C_e) coefficients are expressed by:

$$C_s = \frac{2}{x^2} \sum_{n=1}^{\infty} (2n+1) (|a_n|^2 + |b_n|^2), \quad (4)$$

$$C_e = \frac{2}{x^2} \sum_{n=1}^{\infty} (2n+1) \Re(a_n + b_n), \quad (5)$$

where a_n and b_n are Mie coefficients. The expressions of these coefficients are discussed further by Mishchenko et. al., 2002.

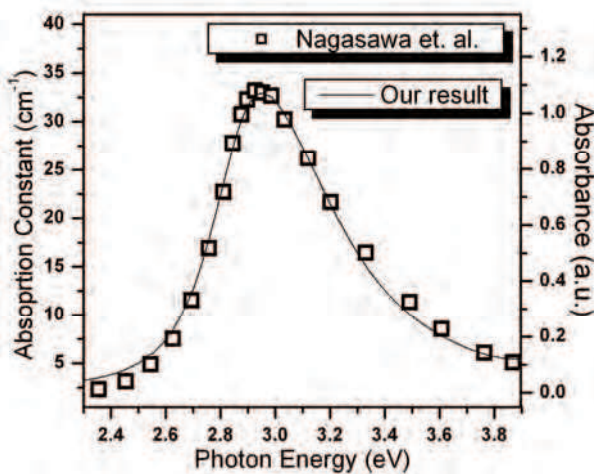


Fig. 4. Absorption spectra of 5 nm ligand-stabilized silver nanoparticles.

The mean value of nanoparticle by analyse of light absorption could calculate by the using presented Mie equations for example using implementation in MiePlot software by Philip Laven (www.philiplaven.com/mieplot). This software estimate the absorption, scattering and extinction spectra for silver, gold and copper nanoparticles.

In the our experiments, we measured absorption for ligand-stabilized silver nanoparticles in cyclohexane. In Fig 4 we show our spectrum and this measured by Nagasawa et. al. 2002.

Perfect agreement between both measurements is seen. The both spectra have maximum about 2.9 eV and similar shape which additionally confirms that we dealt with nanoparticles with mean diameter of 5 nm.

In the recent years, dynamic light scattering was widely used to measure nanoparticles sizes distribution. The DLS is capable to make measurements of particles as small as 10 nm. The advantage of this technique is fast measurement of diameter distribution. In Fig. 5 result of our investigation using DLS is presented. It is characterized by the mean value and standard deviation equal 5.1 nm and 1.1 nm respectively. Results of our measurements confirm that the thermal decomposition method yields narrow distribution of nanoparticles with an average diameter equal to 5 – 6 nm, which is consistent with HRTEM, UV-Vis investigation.

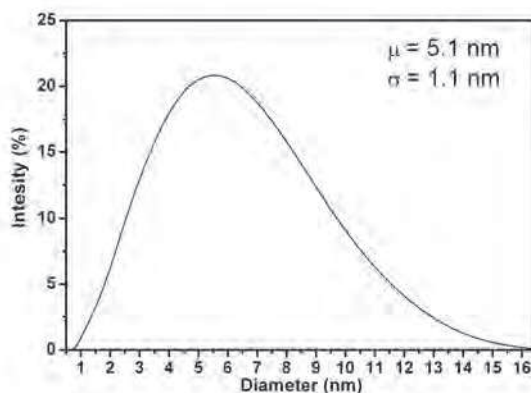


Fig. 5. Ligand-stabilized AgNPs diameter distribution by DLS.

Measurement of size distribution seems to be very important problem. All described techniques returned similar results which is surprising because AFM should measure cores and ligands. From our observations it is clear that it is also not sensitive to the presence of surfactants. We suspect that it is the result of distortion of ligands especially at the core substrate interface. However main advantage of that technique is its locality. Similar advantage could be found in case of HRTEM but here the main problem is related with suspending nanoparticles on special substrates. It in fact allows to measure diameter of the core but this diameter could be completely different after deposition on substrate typical in case of ink jet printing. Here one finds advantages of AFM which can be particularly performed on any substrate.

The two other techniques allows for measurements in solution. Unfortunately interpretation of UV-VIS spectra is not straightforward which makes this measuring technique rather difficult. In contrary the results generated by DLS are in interpretation and the time required for measurement is short which makes this technique the most popular. However it have to be remembered that in case of such measurement results are usually overestimated due to coalescence of the nanoparticles in colloid and also due to influence of not bonded ligands which could increase apparent diameter of the nanoparticles. Therefore, none of the techniques is best nor worst. Each of them could be used to estimate size distribution however experimentalist should always keep in mind limitations related with each of them.

2.2 Analysis of chemical composition

The analysis of chemical composition of nanoparticles seems to be very important task mainly due to two reasons. First of all structure of the surfactants (ligands) could be studied as well as processes related with its desorption (Puchalski et. al. 2009). The other reason is more straightforward – using chemical composition information about quality of the NPs could be deduced and their stability could be predicted. Finally, information about chemical composition is used as a feedback for chemist making synthesis of nanoparticles. In our experiments we have used two most popular and in some sense complementary techniques: energy-dispersive X-ray spectroscopy (EDX or EDS) and X-ray photoelectron spectroscopy (XPS).

EDX could be characterized as a global technique which returns qualitative and quantitative chemical information about investigated sample. Due to relatively large mean free path of X-rays in solid it belongs rather to techniques which could be used to characterize bulk than a surface. However it could be also useful in investigation of nanomaterials especially when they could be prepared in form of a powder. It is the case of AgNPs which could be prepared as a powder. In Fig 6a a EDX spectrum recorded on silver powder is presented. In the middle part of the spectrum five peaks located between 2 keV and 4 keV could be seen. These maxima are related with silver K and L core levels. The maximum which is located at 0.2 keV is related with carbon. The small maximum located at 0.5 keV is related to oxygen 1s characteristic line. The carbon and oxygen signals recorded in our sample indicate the presence of alkyl chains. Beside identification of the elements present in the sample by the use of EDX it is also possible to estimate their concentration. Such analysis is shown in Fig 6b. To obtain quantitative information we used SEMQuant software with implemented ZAF procedure. Analysis of recorded spectra (Fig. 6a) proved high silver contents in silver powder. That contents was evaluated for 74%. Beside that we also estimated amount of carbon and oxygen which contents was estimated to 22% and 4% respectively. This results seems to describe the chemical composition of ligand-stabilised silver nanoparticles with high precision. It is because the 5 nm nanoparticles consist of about 4200 silver atoms (Medasani et. al., 2007) and single ligand (derivative of myristic acid) consist 2 oxygen and 14 carbons atom.

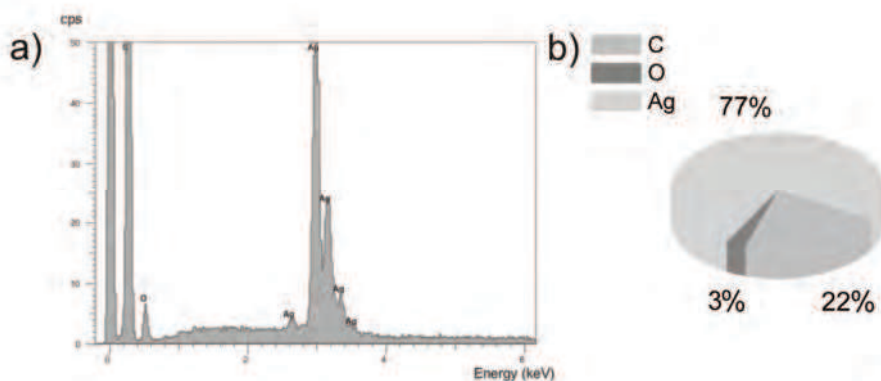


Fig. 6. The results EDX analysis of silver nanoparticles: (a) survey spectrum, (b) quantitative analysis (Puchalski et. al. 2007).

Unfortunately the main problem related with using EDX is related with its global character. To investigate samples with higher precision and in some sense more locally XPS have to be used. This technique is classified as a surface sensitive because a typical analysis depth is limited to the thickness of ~ 7 nm. Because of such attenuation depth it seems to be perfect for performing investigations on clusters and nanoparticles. In Fig. 7a survey XPS spectrum of AgNPs powder is shown. One can see that the most intense lines correspond to the core levels of carbon, silver and oxygen similarly like in case of EDX. This technique could also be used to obtain quantitative information about sample composition (Fig 7b).

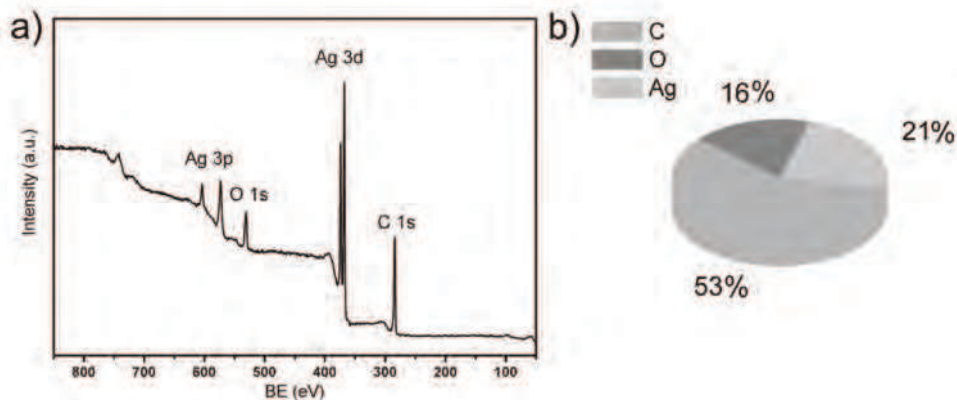


Fig. 7. The results XPS analysis of silver nanoparticles: (a) survey spectrum, (b) quantitative analysis

Our results suggest that sample is composed of 21% of silver, 53% of carbon and 16% of oxygen. These numbers do not agree with similar estimation made using EDX. The main reason for this discrepancy is related with surface character of XPS. It has to be remembered that samples prior loading to UHV were kept in air which resulted in formation of water layer on top of our sample. Such layer is responsible for increase of amount of oxygen in our results. Relatively low amount of silver recorded during our experiment is misleading. Silver is buried under the layer of surfactants which results in screening of the photoelectrons emitted from cores by ligands. As a consequence we are dealing with decreasing of the Ag signal.

The biggest advantage of the XPS is related with its possibility of detecting of chemical bonds which are in the sample. In Fig 8 a C 1s and O 1s core level lines are shown. Vertical lines were added as a guide for an eye and denote location of main components. Carbon C 1s line is dominated by the C-C and C-H signal located at 284.9 eV. The presence of this type of bonds is related to alkyl chains used in our case as ligands. Additionally, carbon-oxygen bonds are detectable: C-O (285.9 eV), C=O (287.3 eV), O-C=O (289.1 eV), which are typical for fatty acids. The oxygen O 1s peak consists of C-O or H₂O (533.2 eV) and C=O (532.2 eV) components. Furthermore, an additional component located at 531.3 eV is seen and in our opinion this could be related to Ag-O-C (531.3 eV) (Gerenser L.J. 1988).

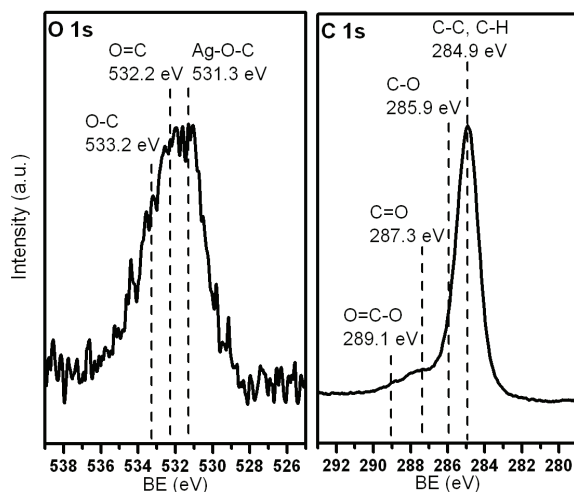


Fig. 8. XPS spectra of O 1s and C 1s core level lines.

2.3 UPS/STS investigations of AgNPs electronic structure

Another techniques which could be used to investigate silver nanoparticles are UPS and STS. Both these techniques allows to investigate electronic structure of materials in vicinity to the Fermi level. Knowledge of electronic structure is very important especially in case of application of materials in electronics. In our investigations we were mainly interested in using of the nanoparticles as a building blocks for conductive tracks formation. Therefore it is reasonable to use these techniques especially to study sintering process which should transfer initially insulating material into conductor. It have to be also pointed out here that both techniques were successively used in studies of quantum size effects which took place in small nanoparticles.

As it was mentioned above we are mainly concentrated on application of silver nanoparticles in Ink-Jet printing in nanoscale electronic. We have decided to investigate the sintering process using STM/STS and UPS. Thus we deposited AgNPs on HOPG (highly oriented pyrolytic graphite) substrate and sintered them in order to create nanometer conductive track. We have decided to use HOPG in these measurements due to two reasons. First of all it is easy to prepare, atomically flat and inert surface. The other reason was related with its semimetallic character. We have expected to observe transition in case of our nanoparticles from insulating state into conducting one. To observe such transition insulating substrate would be the best, unfortunately such substrates are not suitable for UPS and STM measurements thus we decided to select the one with low amount of electronic states located at the Fermi level. The best one in our opinion was HOPG. In Fig. 8 results of our UPS measurements are shown.

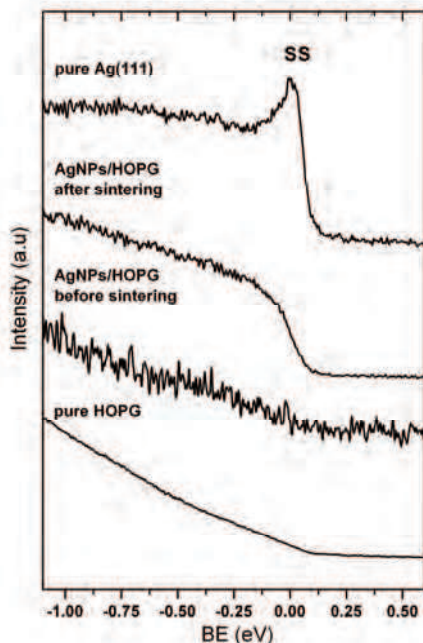


Fig. 8. The comparison of UPS spectra: pure HOPG, AgNPs/HOPG before and after sintering and pure Ag(111).

All spectra were recorded in vicinity to the Fermi level. The pure graphite surface is characterized by soft Fermi edge which resembles its semimetallic character. General shape of the spectrum recorded after deposition of AgNPs is similar to the one recorded on HOPG. The min difference is related with large drop of the intensity recorded on the AgNPs due to insulating character of deposited nanoparticles.

After sintering of NPs at 250°C (after ligand decomposition) the shape of the recorded spectra changed considerably. The distinct Fermi edge could be found which means that surface is covered with metal. It is also clear that obtained spectrum is featureless (see for example the Ag(111) spectrum which has maximum at the Fermi level related with the surface state) which is a clear indication that obtained silver film have polycrystalline character. In order of confirmation of our UPS results we carried out STM measurements on AgNPs deposited on HOPG. Results of these investigations are shown in Fig. 9. We have found out that imaging of NPs deposited on HOPG is extremely hard. In fact during our studies we have been able to record any image which would confirm that we are dealing with nanoparticles on the surface. It is because initially nanoparticles are insulating and STM was designed to investigate conducting or semiconducting materials. However, sintering of the AgNPs changed situation drastically. We have been able to observe large fractal structures composed from small clusters (possibly cores). What is more we measured diameter of individual clusters and it is equal ~5.5 nm which would correspond to presented average diameter of silver core.

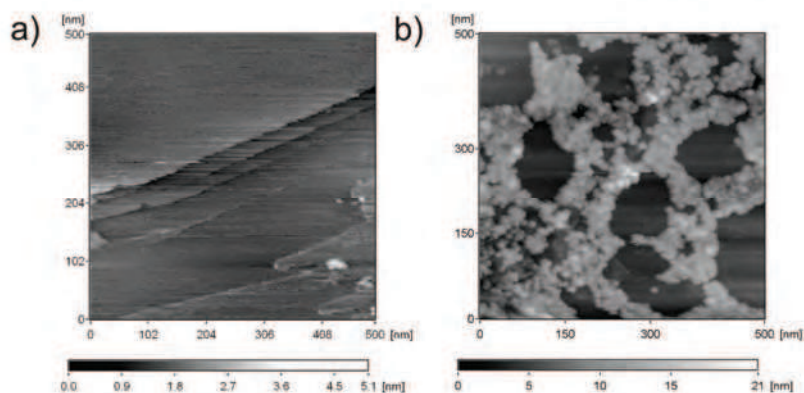


Fig. 9. The STM topography of AgNPs deposited on HOPG before (a) and after (b) sintering at 250°C.

Finally, we decided to use complementary to UPS technique to check electronic structure of obtained Ag film. We performed measurements using scanning tunnelling spectroscopy (STS). Results of these investigations are shown in Fig. 10. The red curve corresponds to a typical $I(V)$ spectrum recorded on HOPG while the blue one on the silver film. It is clear that the curve recorded on Ag film is much steep close to the Fermi level (0 V-bias voltage) which is a measure of number of states at the Fermi level. Thus, we conclude that film which we obtained after sintering of AgNPs is more conductive than HOPG which confirms its metallic character. Furthermore in the Fig. 10b we showed tunnelling conductance maps in which lighter colour corresponds to the region with more electronic states. In some sense, these maps could be interpreted in straightforward way that the lighter areas correspond to more conductive regions of the sample. It is clearly seen that in general Ag is more conductive than surrounding graphite. However, there are still regions with considerably lower number of states than in surrounding regions. It could be related with some amount of ligands which have not been removed completely from the sample. It has to be pointed out here that STS in contrary to UPS allows to investigate sample extremely locally. Because of that these two techniques should be used together to correctly interpret data.

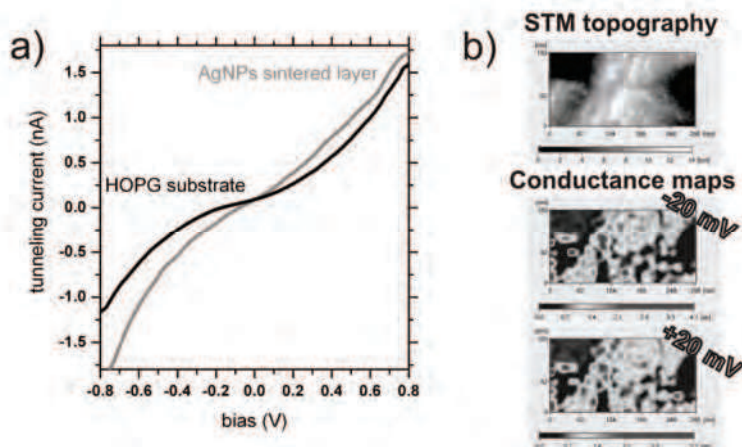


Fig. 10. STS results of AgNPs sintered on HOPG electronic properties investigation. I(V) curve (a) and conductance maps recorded on AgNPs sintered layer on HOPG (b) testify of well conductivity of porous silver fractal aggregates.

3. Summary

The detailed characterisation of nanoparticles is a crucial point in their further application. Without knowledge about their sizes, composition and lengths of ligands nanoparticles could not be used effectively. For example without information about diameters engineers are not able to design jet which with high efficiency would spread nanoparticles on substrate during printing. Without knowledge about composition and length of the ligands it would be difficult to predict what temperature to use during sintering. To learn more about nanoparticles which we are using (commercially available ligand stabilised silver nanoparticles) we have decided to perform series of experiments in order to better understand their properties. We have concentrated here on analysis of AgNPs morphology using HRTEM, AFM, DLS and UV-Vis. Chemical composition was checked using XPS and EDX, and finally electronic structure was investigated using UPS and STS.

The size distribution measured using all four techniques resulted in very similar distribution with average diameter equal 5 nm. This result is especially surprising in case of AFM which should be sensitive also to ligands, therefore expected diameter was equal ~ 8 nm. In our opinion, this discrepancy is the result of distortion of ligands especially at the core substrate interface. Such distortion of ligands could change from one to another substrate which could result in completely different size distributions. From the other point of view the main advantage of that technique is possibility of imaging of individual nanoparticles deposited on different substrates. What is more, the imaging process does not necessary have to be carried out in laboratory but by the use of new portable AFMs could be done in any place particularly in the factory immediately after printing. In contrary HRTEM could be used only in laboratory and investigated material have to be deposited on special substrates. However, no distortion of nanoparticles is expected in case of this technique. Thus, it seems to be most precise one which could be used in diameter estimation. What is

more, extreme magnifications allow to get information about crystallographic structure of prepared nanoparticles. The two other techniques (DLS and UV-Vis) allow for measurements in solution which is their biggest advantage. Unfortunately, interpretation of UV-VIS spectra is not straightforward which makes this measuring technique rather difficult. In contrary the results generated by DLS are simple in interpretation and the time required for measurement is short which makes this technique the most popular. However, it have to be remembered that in case of such measurement results are usually overestimated due to coalescence of the nanoparticles in the colloid. For all these reasons, none of the presented techniques is best nor worst. Each of them could be used to estimate size distribution however experimentalist should always keep in mind limitations related with each of them.

For chemical characterisation of ligand-stabilized silver nanoparticles we have used EDX and XPS. The both techniques give the same results of qualitative analysis of the studied silver powder. The maxima of carbon, oxygen and silver are clearly observed on recorded spectra. Unfortunately, results of quantitative analysis are completely different. Using EDX we recorded relative concentration of main components at the level of 22%, 3% and 75% respectively while in case of XPS 16%, 22% and 53% respectively. The difference originates from large attenuation depth in case of EDX and small one in case of XPS. Thus, EDX could be called bulk sensitive while XPS is surface sensitive. In case of AgNPs powder EDX is a technique which returns expected values of elements concentration. But it would completely fail in case of thin layers of NPs. In contrary XPS does not return correct values but could be successively used for small amounts of NPs. The wrong concentrations of elements returned by XPS are related with shielding of the cores by the ligands as well as by presence of water layer which additionally screens lower deposited layers. Thus, from this point of view XPS is not a good technique for such investigations. But if one knows mean free path of photoelectrons in ligands and cores than is able to calculate length of ligands. This could be the biggest advantage of that technique. Finally, XPS is sensitive to chemical bonds which is another advantage. For example our results confirmed ligand stabilisations of silver core by detection of Ag-O-C bonds (531.3 eV)

Finally we have presented result of our investigations by the use of UPS and STS. Both techniques are used to investigate density of electron states (DOS) in valence band and conduction band (STS only). Interpretation of UPS results is straightforward - recorded signal intensity is measure of DOS while in case of STS it is more difficult due to convolution of DOS with tunneling transmission coefficient. It have to be stressed here that STS is local and UPS global which sometimes disallow for straightforward comparisons of obtained results. In our experiments we have concentrated on investigation of sintering process. Both techniques successively showed that after sintering nanoparticles become conductive. Because local and global character of these two techniques should to be used together to interpret correctly data.

4. Acknowledgments

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