# Mapping near-field plasmonic interactions of silver particles with scanning near-field optical microscopy measurements

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## ABSTRACT

A scanning near-field optical microscope (SNOM) is a powerful tool to investigate optical effects that are smaller than Abbe's limit. Its greatest strength is the simultaneous measurement of high-resolution topography and optical near-field data that can be correlated to each other. However, the resolution of an aperture SNOM is always limited by the probe. It is a technical challenge to fabricate small illumination tips with a well-defined aperture and high transmission. The aperture size and the coating homogeneity will define the optical resolution and the optical image whereas the tip size and shape influence the topographic accuracy. Although the technique has been developing for many years, the correlation between theoretically expected near-field data and measurement is still not convincing. To overcome this challenge, a new information depth is reached containing four optical images at the very same position. Different nanocluster samples with diverse distributions of silver particles are characterized via SNOM in illumination and collection mode. This will lead to topographical and optical images that can be used as an input for SNOM simulations with the aim of estimating optical artifacts. Including tip, particles, and substrate, our finite-element-method simulations are based on the realistic geometry. Correlating the high-precision SNOM measurement and the detailed simulation of a full line scan will enable us to draw conclusions regarding near-field enhancements caused by interacting particles.

**Keywords:** scanning near-field optical microscopy, plasmonic interactions, silver nanoparticles, SNOM probe, FEM simulation, near field, optical artefacts

## 1. INTRODUCTION

Nanoparticle systems are widely used in industry and research due to their unique optical properties [1-3]. Owing to the growing importance of plasmonics [4], metal silver nanoparticles found considerable scientific interest [5], last but not least because of the combination of far-field scattering and near-field concentration. Even though the topic is by no means new, there are many details of the interaction between metal nanoparticles requiring further studies. In the experimental field of research, the affordable synthesis of regular particles is problematic, even if there are small-scale high-vacuum techniques to produce a regular pattern e.g. focused ion beam or techniques like nano imprinting. To successfully implement nanoparticles in large-area devices such as solar cells or light sources, a fabrication method is needed allowing controllable particle sizes. In this paper, we will use the annealing of silver particles produced with nanosphere lithography [6]. The metal nanoparticles have a very homogenous radius and shape, however at the boundaries the particle distribution is irregular. These imperfections permit us to investigate different interactions.

Scanning near-field optical microscopy (SNOM) is a powerful tool [7] to investigate the optical response of nanostructures. Not only the optical near-field behavior can be investigated but also the topography is measured at the same time. Although there are many topographical and optical artefacts [8] that can appear in the measurement, aperture SNOM is one of the best techniques to obtain an optical image and a better understanding of electric field distributions that can interact with other optical-active particles or layers [9]. The main reason for the limitation of the optical and topographical resolution is a strong dependency on tip shape and on properties of the incoming light. The way we want to provide a solution to estimate deviations is the usage of a simulation that takes into account a realistic measurement geometry. In particular, this includes the tip, particles, and substrate. We will discuss how different tip shapes, particle spacing, and measurement parameters can affect the optical image. Providing the influence of critical measurement parameters, we will improve the SNOM set-up and discuss the resolution of the resulting image.

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## 2. METHODOLOGY

Originating from recent publications in the field of near-field optics [10-12], the strong need of interpreting aperture SNOM images becomes clear [13]. Although simulation data are existing [14], the near-field interaction of tip and particle was not systematically taken into account. The influence of a free-standing tip was already investigated [15] and particle near-field interactions in air [16] or on a substrate have been calculated [17]. To discuss an optical image of a sample with different nanoparticle distributions and field effects, this study will show how 2D numerical finite-element-method (FEM) simulations can contribute a new approach to reconstruct the original particle situation. The following parameters could influence the optical image:

- tip-particle distance
- particle interactions (near field / far field)
- deformation or particle residues at the tip

Already existing studies [14] show that the tip coating is an important factor, but just for the case that the tip is very good or completely damaged, for a normal tip that was already used serval times the optical images changes little. Our simulation will focus on a symmetric tip with a large aperture of 100 nm diameter and a coating thickness of 200 nm estimated from SEM images. The tip condition is observed by the propagation light from the tip. Higher emittance at the tip opening can be attributed to a damaged coating. Figure 1 shows a image of the set-up with an aperture tip in illumination mode glued onto a tuning fork placed from behind on a sample of silver nanoparticles on a glass substrate. The bright light spot in front of the tip originates from the 532 nm LASER light coupled into a single-mode pulled glass fiber coated with an aluminum layer. This set-up is translated into a simulation model with an Al-coated glass tip on a silver particle on a glass substrate. The electromagnetic wave is coupled into the fiber via a port inside the fiber model and two simulations with and without particle are calculated.

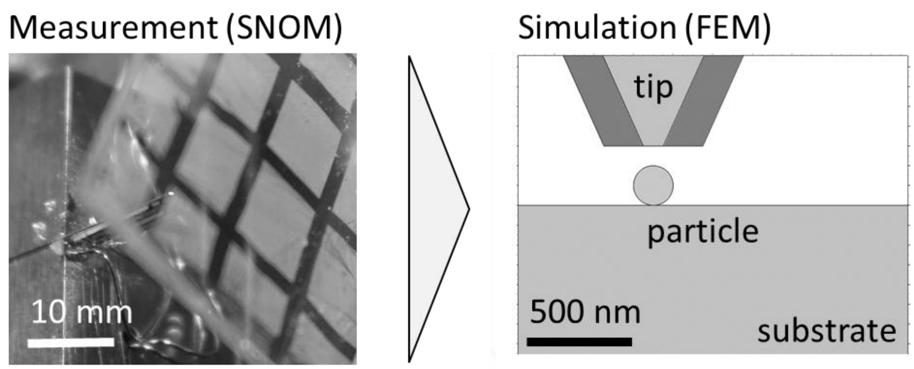


Figure 1. Comparison between real set-up and simulation input. Left side: tuning fork with glass fiber tip (laser light propagation) illuminating from behind the glass sample with silver nanoparticles. Right side: tip (glass, Al), particle (Ag) and substrate (glass) in simulation cross section.

**SNOM measurement**

The SNOM measurement is done with a set-up suiting our individual requirements [13]. In shear-force mode, the tip is in contact with the surface and exerts an adjusted force on the sample. With three detectors, the set-up is flexible enough to investigate optical information of the sample in serveral configurations at the very same position:

- Illumination mode: transmission and reflection (simultaneous)
- Collection mode: transmission
- Collection mode: reflection

The detectors for the optical measurements are mounted at 180° with respect to the sample normal for transmission measurements and at 55° (right-hand side) for reflection measurements. The illumination in the collection mode is done with 180° incidence for transmission and 315° (left-hand side) for reflection measurements. The detector is then coupled with an SMA connector to the spectrometer. The topographic images are calibrated with a standard calibration grating to normalise the x,y,z dimensions of the measurement. With an image processing software [18], the data are levelled by subtracting the averaged plain and the number of pixels is increased. A standard measurement has a pixel size of 200 x 200 and a step width of 25 nm. Optical data were not post processed.

**Finite-Element-Method (FEM) simulation**

FEM simulation is a numerical technique to compute boundary conditions of small subdomains called finite elements. The method helps to solve a complex geometry with an initial function, which is entered into differential equations. We calculate the time-harmonic electromagnetic field distribution of our model with the response of the linear model subjected to harmonic excitation for one frequency. Our FEM simulations (using the software package COMSOL Multiphysics™) are currently limited to 2D to estimate the most critical influence parameter before extending to 3D simulations. The polarisation of an aperture tip strongly depends on the shape of the tip opening [19]. We will assess this with the optical images we observe and have to rotate the image to compare it with the simulation. For all simulations the power of 1 W is inserted with a 750 nm large port situated at a distance of three times the wavelength above the tip opening. The maximum mesh size is 30 nm and the simulation boundary is formed by a rectagular PML layer system. The overall box size is 4 µm x 4 µm. The silver particle size is 100 nm in radius, the tip aperture has a diameter of 100 nm and the aluminium coating has a thickness of 200 nm. The transmission data is achieved by integrating the power flow over all glass/PML boundaries. The difference between the simulation with and without particle is calculated to reduce the influcence of the boxsize, mesh effects and small PML reflections. To obtain a complete SNOM image, the tip is maximally moved by 50 nm per step over the particle in constant high mode. Our prior simulations show that there is no significant change by using a constant gap mode simulation apart from edges or movements in between the particles, which is not the case for gaps that are smaller than the overall tip (tip aperture and two times tip coating).

## 3. DATA AND ANALYSIS

In this section, we will show the results of SNOM measurements and related simulations. Therefore, we will take a particle cluster and estimate the real particle situation that cannot be measured by the aperture tip due to the size ratio between tip and particles (the tip is many times larger than the particles). The measured data will be followed by a parameter study of the tip-sample interactions and the determination of the efficiency range of one silver nanoparticle, which is essential to understand near-field and far-field interactions.

**SNOM measurement**

As already stated, the topographic resolution of the SNOM image is limited by the tip geometry. On the other hand, the optical resolution is not limited by this, because of the smaller aperture size and the tips near field, which is a field distribution and will be very sensitive to a changing surrounding. Even if the tip is deformed or affected by the coating, the near-field change of the particles can still be measured. A possible issue is then the interpretation of the optical image [20].

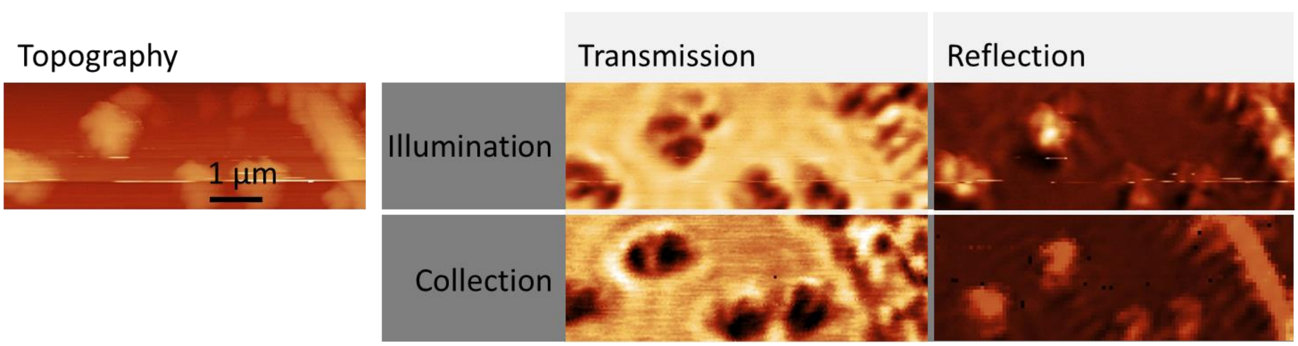


Figure 2. Measurements of transmission and reflection in illumination mode (top) and transmission and reflection in collection mode (bottom) together with the topography (left) for the same position. Bright color: high counts or high values, dark color: low counts or low values, scale bar of topography is also valid for optical images.

To overcome this challenge, we already established a model to determine the optical synergy of reflection and transmission image in illumination mode and a normalisation method [13]. In Figure 2, the transmission and the reflection image of the collection mode at the very same position is shown to further enrich the information depth of the optical images.

The topography shows four huge particles that we would not expect from SEM image of this sample showing silver nanoparticles with a radius of 100 nm. On the right side, the particles accumulated to form an array caused by the preparation method of the nanoparticles. The optical transmission images indicate that clusters of particles are measured because of the irregular field enhancements. Much smaller particles and roughness within the glass substrate are not considered in the following. It could be clearly observed that there is a strong interaction between clustered particles. Transmission and reflection images show interactions which are known for non-isolated particles [21].

The optical images strongly suggest the need of simulations, because the optical images do not match with the topographic measurement whose resolution is not good enough to separate different particles. In this paper, we will concentrate on transmission images caused by high contrast of optical information, which has to be improved in the reflection data for the collection mode. In principal the predictive value of a reflection image can be higher due to the higher near-field/far-field ratio [22].

**FEM simulation**

On the basis of SNOM measurements, we are interested in interactions of particles and the far-field scattering that enables the particle to interact with light in a range larger than its diameter. The theory implies that the near field decreases inversely proportional to the square of the radius. In the following simulations (Figure 3) the tip is moved across the glass surface and the transmitted average power flow is detected for each tip position. The x scan position 0 nm is indicated in the sketches in every subfigure (Figure 3) by a dashed grey line.

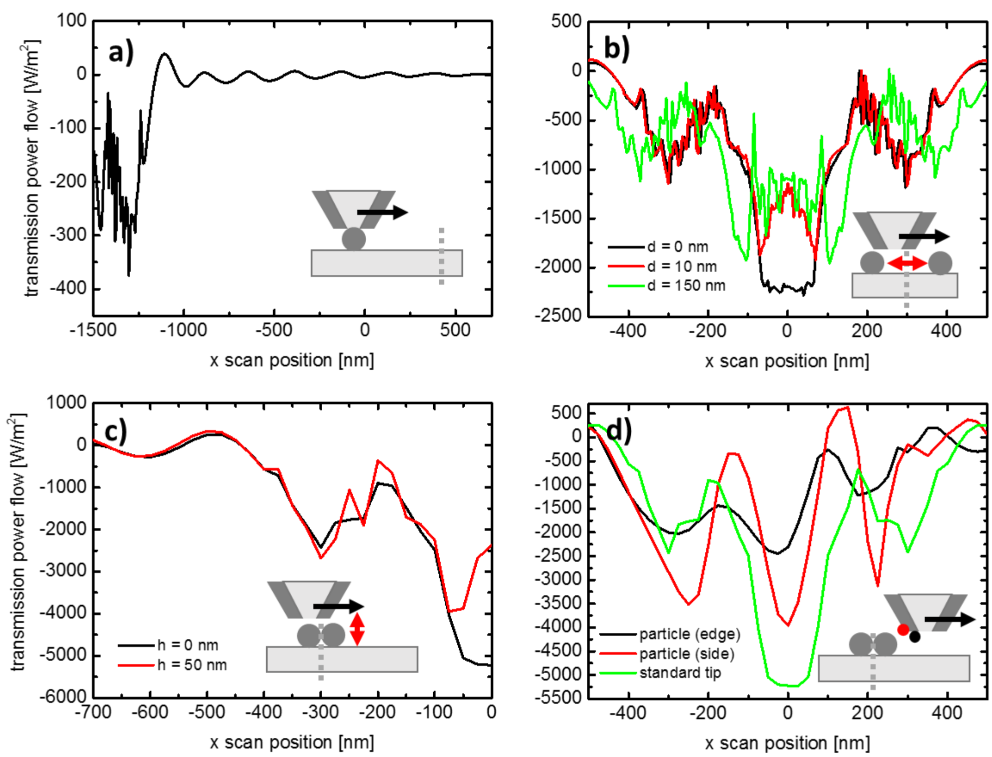


Figure 3. Simulated transmitted average power flow for situations as depicted in the insets (dashed gray line = 0 nm x scan position): a) tip laterally moving away from the nanoparticle. b) two separated particles with a spacing d. c) two particles with different tip-particles distance h. d) tip shapes (with particles (d = 25 nm) attached) color of the particles suits to line color.

In the figures, h is the gap size between particle and tip, and d is the spacing between two particles. If it is not mentioned differently h is 0 nm and the radius of the particles is 100 nm. Figure 3a shows a tip-nanoparticle interaction. The tip moves away from the particle position at -1500 nm. After the centre of the tip opening reached -1250 nm the tip is not in contact with the particle anymore, which can be recognised by a strong peak. The coating of the tip continues the interaction over 250 nm and ends up in a typical wave pattern of an airy disk. Thereby, the particle and its near-field are able to influence the electric field further than 1 µm.

The presence of a tip can also change the particle-particle interaction by forming a particle-tip-particle bridge configuration. In Figure 3b, the simulation result indicates that closely packed particles (d = 0 nm) in contact with the tip have no field enhancement in the gap. By moving the particles apart from each other with a gap size of 10 nm, in theory the particles show strong enhancements [21]. This can be measured by the tip but the measured normalised intensity on top of the gap is not as high as expected (more than 0). If we pull the particles even further apart to a distance of 150 nm, the particles will show a strong field enhancement that is measurable with the tip and the near fields will start to become independent from each other. Yet, a particular interaction area can still be seen between the two peaks at -100 nm and 100 nm, which is in accordance with the simulation in Figure 3a.

The tip height cannot be defined precisely in the experimental measurement. Figure 3c shows the difference between contact and non-contact mode. The maximum peak position stays the same while the interaction between two connected particles can be distinguished by the non-contact mode. That implies that the non-contact mode gives more information about the composition of nanoclusters, but can also impede the interpretation with interacting near fields. If we succeed in further research to combine both constant-gap and constant-height mode, the near-field characterisation can get even more precise. The sub-structure of the peaks in Figure 3c and in Figure 3b cannot presently be explained. We can imagine that it is an interaction between all particles and different tip positions. Further simulations will show, which tip parameters will affect the structure and clarify whether there is an interference and where it originates from.

The coating of the pulled tip is sensitive to deformations. All simulations attribute an important role to the tip, so that it is necessary to check the influence of the tip sample-distance and the tip shape. We will focus on an attached particle, however other tip-geometry issues can be considered. In the situation of a shear force scanning mode, there is a likelihood that a small particle will attach to the tip. This could be either explained by electro-static forces or by the deformation of the tip coating. Figure 3d depicts the change of a normal tip with an attached particle on the edge or at the side of the tip. Both situations are illustrated in the inset of the diagram. An asymmetric tip shape will result in an asymmetric field measurement and will decrease the intensity contrast in the image. The asymmetric near-field distribution of the tip will interact with the particle and then enhance both sides differently. Therefore, the tip interacts with the closest part of the tips coating and the system, so that the first particle is not affected by the tip damage. The particle feels the strongest field that is available and interacts with it. Due to the strong field, when the tip is on top of the particle, the field of the attached particle is too weak to affect the measurement.

In all cases, we can conclude that we do not measure the pure near-field effects of the particles but rather a change in the near-field distribution of the system (particles, tip), coupled with a far-field scattering of the nanoparticles. Theoretically, the near-field can only propagate if there is an aperture close to it. Additionally, in the measurements and from the simulation we know that the antenna/detector principle is modified by other particles or by the tip itself.

## 4. RESULTS

Following the interpretation of SNOM measurements and FEM simulations, we combine the effects that were identified by the systematic study of particle interactions. The line scan (transmission in illumination mode) of a particle cluster, taken from Figure 2, can be seen in Figure 4. The experimental data are plotted as black symbols and show a boundary of the particle system. In the simulation this can be seen for values above 0 $W/m^2$ and in the experiment there is small enhancement before the counts level off at about 0.95 counts (normalised).

Within the range of 500 nm to 2000 nm there is a field enhancement that cannot be related to height changes of the tip, because the topography in Figure 2 is the feedback signal of the height position which is constant in this range. The enhancement must be based on a near-field interaction between particles. We already know that the measured particles have a size of a few hundred nanometres and so we take two closely packed nanoparticle formations into consideration. Both minima point to connected particle interaction and the simulation is built with three and two particles, respectively. For an unknown sample minima could also be caused by a large elongated particle, but we know from the fabrication method and SEM analysis that the particles have a spherical shape and a uniform size. The green line in Figure 4 adds the simulation data. It is calculated for a glass substrate, a standard tip shape and five particles that are distributed as mentioned before. The distance between the particle clusters is estimated from the transmission measurement.

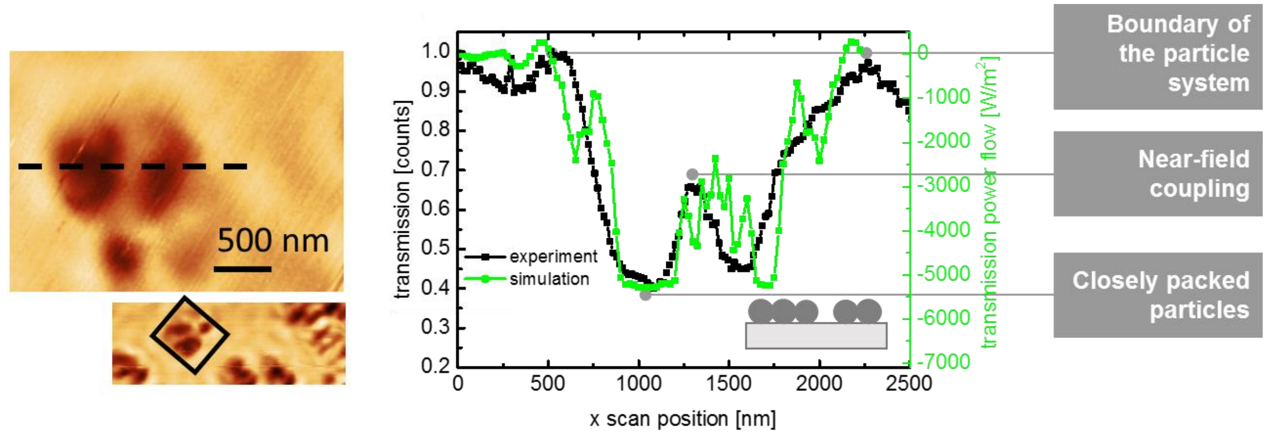


Figure 4. Section of a SNOM transmission measurement in illumination mode and its cross section (dark line) compared to a simulation of five particles (light line).

The comparison between measurement and simulations shows a high consistency. However, the substructure of the simulation is much finer than the measurement and contains more information about the particle system. That can be explained by the low contrast and large integration time with respect to scanning speed or a low signal to noise ratio of the charge-coupled device (CCD) detector in the measurements. The fine structure of the simulation demonstrates that the particle-particle interactions must be investigated closer by particle size studies and the measurements must be improved by a more efficient CCD detector. The measurement has got asymmetric slop on both boundary sides, which is a tip influence of a non-perfect tip shape.

## 5. CONCLUSION

We showed that SNOM measurements need a high optical information depth and a simulation study to investigate and interpret optical data sets. Therefore, we measured silver nanoparticles on a glass substrate with an aperture SNOM in illumination and collection mode to detect both reflection and transmission, respectively. The optical resolution is surpassing the topography as it is not limited by the coating thickness of the tip. Supporting case studies of simulations, helped to understand tip-particle, particle-particle and bridging interactions and can be used to build a simulation that gives an evidence how the particle cluster can look like. This convincing conformity can be improved by more studies of tip and particle parameters such as coating thickness, coating roughness, wavelength dependency and particle diameter. Simulations will be expanded to compare also other modes of the measurement.

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## REFERENCES

[1] F. Kretschmer, S. Muhlig, S. Hoeppener *et al.*, "Survey of Plasmonic Nanoparticles: From Synthesis to Application," Particle & Particle Systems Characterization, 31(7), 721-744 (2014).

[2] P. D. Howes, S. Rana, and M. M. Stevens, "Plasmonic nanomaterials for biodiagnostics," Chemical Society Reviews, 43(11), 3835-3853 (2014).

[3] O. Hess, J. B. Pendry, S. A. Maier *et al.*, “Active nanoplasmonic metamaterials,” Nature Materials, 11(7), 573-584 (2012).
[4] H. A. Atwater, and A. Polman, “Plasmonics for improved photovoltaic devices,” Nature Materials, 9(3), 205-213 (2010).
[5] Y. C. Chang, H. W. Chen, and S. H. Chang, “Enhanced Near-Field Imaging Contrasts of Silver Nanoparticles by Localized Surface Plasmon,” IEEE Journal of Selected Topics in Quantum Electronics, 14(6), 1536-1539 (2008).
[6] J. C. Hulteen, D. A. Treichel, M. T. Smith *et al.*, “Nanosphere lithography: Size-tunable silver nanoparticle and surface cluster arrays,” Journal of Physical Chemistry B, 103(19), 3854-3863 (1999).
[7] D. Richards, “Near-field microscopy: throwing light on the nanoworld,” Philosophical Transactions of the Royal Society of London Series a-Mathematical Physical and Engineering Sciences, 361(1813), 2843-2857 (2003).
[8] B. Hecht, H. Bielefeldt, Y. Inouye *et al.*, “Facts and artifacts in near-field optical microscopy,” Journal of Applied Physics, 81(6), 2492-2498 (1997).
[9] B. Hecht, B. Sick, U. P. Wild *et al.*, “Scanning near-field optical microscopy with aperture probes: Fundamentals and applications,” Journal of Chemical Physics, 112(18), 7761-7774 (2000).
[10] B. J. Bohn, M. Schnell, M. A. Kats *et al.*, “Near-Field Imaging of Phased Array Metasurfaces,” Nano Lett, 15(6), 3851-8 (2015).
[11] A. V. Ankudinov, A. M. Mintairov, S. O. Slipchenko *et al.*, “Scanning Near-Field Optical Microscopy of Light Emitting Semiconductor Nanostructures,” Ferroelectrics, 477(1), 65-76 (2015).
[12] M. K. Hossain, M. Kitajima, K. Imura *et al.*, “A Topography-Metrology Correlation in Nanoscale Probed by Near-Field Scanning Optical Microscopy,” Plasmonics, 10(2), 447-454 (2015).
[13] P. Andrae, P. Fumagalli, and M. Schmid, “Comparative scanning near-field optical microscopy studies of plasmonic nanoparticle concepts,” Proc. of SPIE, 9132 (91320F-1), (2014).
[14] L. Novotny, D. W. Pohl, and P. Regli, “Near-Field, Far-Field and Imaging Properties of the 2d Aperture Snom,” Ultramicroscopy, 57(2-3), 180-188 (1995).
[15] L. Novotny, D. W. Pohl, and B. Hecht, “Scanning near-Field Optical Probe with Ultrasmall Spot Size,” Optics Letters, 20(9), 970-972 (1995).
[16] M. Schmid, P. Andrae, and P. Manley, “Plasmonic and photonic scattering and near fields of nanoparticles,” Nanoscale Research Letters, 9, (2014).
[17] E. M. Atie, Z. H. Xie, A. El Eter *et al.*, “Remote optical sensing on the nanometer scale with a bowtie aperture nano-antenna on a fiber tip of scanning near-field optical microscopy,” Applied Physics Letters, 106(15), (2015).
[18] D. Nečas, and P. Klapetek, [Gwyddion], http://gwyddion.net/, (25.12.2014).
[19] S. Werner, O. Rudow, C. Mihalcea *et al.*, “Cantilever probes with aperture tips for polarization-sensitive scanning near-field optical microscopy,” Applied Physics a-Materials Science & Processing, 66, S367-S370 (1998).
[20] P. J. Dobson, “Handbook of Nano-optics and Nanophotonics,” Contemporary Physics, 56(2), 244-245 (2015).
[21] J. A. Fan, C. H. Wu, K. Bao *et al.*, “Self-Assembled Plasmonic Nanoparticle Clusters,” Science, 328(5982), 1135-1138 (2010).
[22] V. Sandoghdar, S. Wegscheider, G. Krausch *et al.*, “Reflection scanning near-field optical microscopy with uncoated fiber tips: How good is the resolution really?,” Journal of Applied Physics, 81(6), 2499-2503 (1997).