Silver Coated Platinum Core–Shell Nanostructures on Etched Si Nanowires: Atomic Layer Deposition (ALD) Processing and Application in SERS


A new method to prepare plasmonically active noble metal nanostructures on large surface area silicon nanowires (SiNWs) mediated by atomic layer deposition (ALD) technology has successfully been demonstrated for applications of surface-enhanced Raman spectroscopy (SERS)-based sensing. As host material for the plasmonically active nanostructures we use dense single-crystalline SiNWs with diameters of less than 100 nm as obtained by a wet chemical etching method based on silver nitrate and hydrofluoric acid solutions. The SERS active metal nanoparticles/islands are made from silver (Ag) shells as deposited by autometallography on the core nanoislands made from platinum (Pt) that can easily be deposited by ALD in the form of nanoislands covering the SiNW surfaces in a controlled way. The density of the plasmonically inactive Pt islands as well as the thickness of noble metal Ag shell are two key factors determining the magnitude of the SERS signal enhancement and sensitivity of detection. The optimized Ag coated Pt islands on SiNWs exhibit great potential for ultrasensitive molecular sensing in terms of high SERS signal enhancement ability, good stability and reproducibility. The plasmonic activity of the core-shell Pt//Ag system that will be experimentally realized in this paper as an example was demonstrated in numerical finite element simulations as well as experimentally in Raman measurements of SERS activity of a highly diluted model dye molecule. The morphology and structure of the core-shell Pt//Ag nanoparticles on SiNW surfaces were investigated by scanning- and transmission electron microscopy. Optimized core–shell nanoparticle geometries for maximum Raman signal enhancement is discussed essentially based on the finite element modeling.

Surface enhanced Raman spectroscopy (SERS) is a technique that was developed to detect extremely small quantities of molecules by determining their characteristic Raman signal, that is, their characteristic vibrational modes.[1–3] To make use of the Raman signal enhancement nanoscopic noble metal particles in colloidal solution[4] or on substrates are usually used.[5,6] These metallic nanoparticles exhibit collective oscillations of the free-electron gas on the particle surface, called localized surface plasmons (LSP), excitable by the direct coupling to the incident light. Due to the strong confinement of the evanescent fields onto the nanoscale, plasmons are accompanied by large electric field enhancements in the direct vicinity of the particle surfaces. Correspondingly, the high sensitivity of SERS has a mainly electromagnetic origin described via the locally enhanced electric field that can be used to excite vibrational modes in the molecules adsorbed on the noble metal nanoparticles. In the same manner the radiated Raman signal will be plasmonically enhanced. As a rule of thumb one can use the fourth power of the local electric field enhancement factor for an estimation of the expected SER intensity enhancement.[7,8] Plasmons can best be excited by laser light in noble metal [e.g. gold (Au), silver (Ag)] nanoparticles and nanostructures which are therefore very well suited to serve as active substrates for SERS. Particular strong intensity enhancements are expected at positions where adsorbed molecules (adsorbs) stay in close vicinity (a few nanometers apart, at most) to the so-called hot spots, points of strong field enhancement in between the gap region of noble metal nanoparticle dimers. However, noble metal particles are usually inhomogeneous in size and shape, for example, the small Au particles on a Si substrate, which are produced by annealing a thin (few nanometers thick) Au layer that decomposes into nanoscale Au droplets, show a broad size distribution and exhibit a lens shape[9] instead of the, for signal enhancement, more desirable hemispherical, elliptical or rodlike shapes.[10] These inherent disadvantages of the conventional SERS substrates are circumvented by using the hemispherical gold droplets atop silicon nanowires (SiNWs) as they occur during the vapour–liquid–solid (VLS) growth[11,12] of semiconductor nanowires (NWs). Also,

[1] Dr. V. A. Sivakov, K. Höflisch, Dr. M. Becker, Dr. A. Berger
Max Planck Institute of Microstructure Physics
Weinberg 2, 06120 Halle (Germany)
Fax: (+49) 3641 206 499
E-mail: vladimir.sivakov@ipht-jena.de
[2] Dr. V. A. Sivakov, K. Höflisch, Dr. M. Becker, Dr. A. Berger, Dr. T. Stelzner, Dr. S. H. Christiansen
Institute of Photonic Technology
Albert-Einstein Str. 9, 07745 Jena (Germany)
[3] Dr. K.-E. Elers
Picosun Oy
Tietotie 3, 02150 Espoo (Finland)
[4] Dr. V. Pore, Prof. Dr. M. Ritala
University of Helsinki, Department of Chemistry
PO Box 55, 00014 Helsinki (Finland)
[5] Dr. S. H. Christiansen
Max Planck Institute for the Science of Light
Günter-Scharowsky Str. 1, 91058 Erlangen (Germany)
welding a SiNW with a Au droplet onto an AFM tip yields a probe for tip enhanced Raman spectroscopy (TERS). By realizing core–shell metallic nanoparticles for example, with different metals in core and shell, and different shapes/dimensions of core and shell it is possible to tune the materials optical properties such as extinction spectra to be more resonant with the vibrational modes of the adsorbents/analytes of interest. Atomic layer deposition (ALD) is a method that enables controlled deposition of highly conformal and uniform thin films. However, in the case of noble metal ALD, continuous film deposition is hindered essentially when a low number of ALD deposition cycles are applied. Due to difficult nucleation, nanoparticles rather than thin films form. The problem of poor nucleation is emphasized when depositing with ALD on high aspect ratio structures like SiNWs because of the low partial pressure of the precursor within the structures compared to the partial pressure on planar substrates. The nanoparticle formation using ALD of ruthenium (Ru) has already been exploited in preparation of nanoparticle based nonvolatile memories and for metallization of aerogels. Pt nanoparticle growth by ALD has in turn been explored for catalytic purposes. The main problem of using ALD nanoparticle deposition to be employed in the field of plasmonics is a lack of easy to use processes for the most suitable metals in this field, that is, silver and gold. Only a single report exists on radical enhanced ALD of silver and even if the films had reasonably low resistivity of 6 $\mu$S/cm, they contained quite substantial amounts of impurities. In this paper we will discuss the formation of plasmonically active silver (Ag) coated ALD deposited platinum (Pt) nanoparticles, that is, core-shell nanostructures (for short: Pt//Ag core-shell nanoparticles) on Si nanowires (SiNWs) mediated by ALD technology. The morphology and structure of the core–shell nanoparticles on SiNW surfaces was investigated by scanning and transmission electron microscopy and will be discussed in detail. The optimum geometry for maximum field and Raman signal enhancements in metal Pt//Ag core–shell nanoparticles on SiNWs will be discussed essentially based on numerical finite element modeling. The plasmonic activity of the core–shell Pt//Ag system was demonstrated in numerical simulations as well as experimentally in measurements of SERS activity of a highly dilute model dye molecule, that is, methyl violet, deposited onto the Pt//Ag on SiNW system.

The SiNWs were realized by the wet-chemical etching of silicon (Si) wafers (Si(111), 5–10 $\Omega$ cm). For the etching procedure, a mixture of 0.02 mol silver nitrate (AgNO₃) and 5 mol hydrofluoric acid (HF) in the volume ratio 1:1 was applied for 30 min at room temperature and atmospheric pressure. The etching process is based on the galvanic displacement of Si thereby oxidizing the Si to form silicon dioxide (SiO₂) so that the HF component of the solution can remove the SiO₂ and in parallel by reducing the silver ions (Ag⁺) to metallic silver (Ag⁰) at the Si surface. Pt nanoparticles were deposited onto the SiNW surfaces in a controlled ALD process using a commercially available ALD reactor (SUNALE R-150 ALD reactor, Picosun Oy) with methycyclopentadienyl-trimethyl-platinum (MeC₅H₄PtMe₃) and oxygen (O₂) as precursors. The platinum metal–organic precursor was evaporated at 40°C and the growth of platinum nanocrystallites/islands on SiNWs was observed at a substrate temperature of 300°C. For each ALD growth cycle the oxidizing agent in the form of oxygen was pulsed for 0.7 s (purge 10 s) and the MeC₅H₄PtMe₃ precursor was pulsed for 1 s (purge 10 s). The cycle number applied for the formation of platinum nanoparticles/islands on etched SiNWs surfaces was 300 for each deposition process. The specifics of the Pt island ALD growth process was discussed in details by Aaltonen et al. For the formation of Ag shells around the Pt islands an automaticallographic technique was used. Therefore, the samples were treated with a mixture of 150 μL silver lactate (0.022 g in 3 mL de-ionized H₂O) plus 100 μL citrate buffer (1.275 g citric acid plus 1.175 g tri-sodium citrate dihydrate in 5 mL de-ionized H₂O) plus 150 μL hydroquinone (0.17 g in 3 mL deionized H₂O) for 2 min. Structural analysis of the etched and decorated SiNW surfaces has been carried out by field emission scanning electron microscopy (FESEM) and high resolution transmission electron microscopy (HRTEM) using a FEI CM200/UT machine. The scanning energy-dispersive X-ray maps were obtained using a Philips CM20FEG scanning TEM instrument equipped with an EDX detector (IDFix-system, SAMx). The Raman measurements making use of the SERS effect at plasmonically active nanoparticles such as Pt//Ag islands to reside in a high density on SiNWs were carried out using the dye molecule methyl violet (C₅H₇NO₂S, $5 \times 10^{-5}$ mol L⁻¹). The SERS mappings were carried out with a Jobin Yvon LabRam HR800 spectrometer. For excitation, the 514 nm emission line of an Ar⁺ ion laser was used. The laser power was 0.8 mW and the focused laser spot on the sample surface was 2 μm in diameter, that is, the resulting energy density within the spot was 2.5 x 10⁴ W cm⁻². The incident beam was along the normal of the substrate surface and the backscattered signals were collected along the opposite direction. The integration time for all measurements was 20 s. Finite element (FE) modeling provides a powerful tool for the numerical solution of partial differential equations in variable geometries. In this work the commercial COMSOL software package (see: http://www.comsol.com for further information) is used to solve the classical scattering problem in electro-dynamics. For the solution of the Helmholtz equation the material response is taken from thin film data for Ag[42] and Pt[43] The simulations are restricted to two-dimensional (2D) models of dimer nanoshell cylinders so that fast and reliable modeling can be assured. However, all necessary physical principles and materials properties are included. In the framework of simplified 2D models, simulations show the plasmonic activation of the Pt nanoparticles/islands via selective deposition of a nanoscale Ag shell. Moreover, this dimer configuration is closest to the real structures and still comparable simple, showing the formation of a hot spot in the gap between the nanoshell cylinders which is assumed to be crucial for the enormous Raman signal enhancements. The standard geometry consists of a circular calculation domain with a diameter of 1.5 μm surrounded by a perfectly matched layer to avoid any backscattering from the boundaries. The dimer inside the calculation domain is composed of two well separated cylinders with plat-
inum cores of 10 nm radius, with a spacing of 2 nm with the dimer axis being oriented along the x-direction. For the investigation of the influence of an additional silver shell several models were set up with silver shell thicknesses from 2 up to 10 nm in two nanometer steps by maintaining the 2 nm spacing in-between the dimers. The shells are described by their inner and outer radii in brackets \((r_1, r_2)\), with \(r_1\) being the radius of the Pt core and \(r_2\) the radius of the silver shell in nanometers. The incident electric field is normalized and it propagates in the y-direction while its polarization points along the dimer axis. The latter ensures the maximum coupling between the cylinders and therefore results in the highest possible field enhancement. The electric field enhancement factor, a dimensionless quantity as used in Figure 6 is defined by \(E_{\text{peak}}\) that is, the local electric peak value divided by \(E_{\text{inc}}\), the incident electric field. Values larger than 1 represent a local field enhancement. Even though 2D models provide for some physical insights, one should keep in mind that cylinders show slightly modified resonance positions\(^4\) and weaker field enhancements compared to spheres, which would be more appropriate to describe the deposited core–shell nanoparticles/islands (cf. the TEM micrographs in Figure 1 and Figure 2). Thus, any estimation of the expected field enhancement based on these FE models, yields a lower boundary for the achievable SERS enhancements in the experiment.

Wet chemical etching of Si(111) wafer surfaces by solutions containing HF and AgNO\(_3\) (as was specified in the experimental section) results in the formation of vertical SiNW architectures as visible in the SEM and TEM micrographs in Figure 1.

The as prepared SiNWs are perpendicular to the wafer surface and have very rough surfaces compared to SiNWs grown bottom up by the vapour liquid solid growth process.\(^{44, 45}\) The diameter of the etched SiNWs lies between 30 and 200 nm at a typical SiNW length of \(\sim 5\ \mu\text{m}\) (cf. Figures 1a, b). The morphology investigations of the etched SiNWs in the SEM and TEM after Pt island deposition are presented in Figures 1c, d. These micrographs show that the SiNW surfaces are densely covered with nanoscale Pt nanoparticles/islands at diameters of 5–15 nm. The spacing of Pt islands shows a distribution so that some islands are dense enough to be able to electromagnetically couple to neighbouring islands while others are too far apart to be able to do the same. Here, further optimization of the ALD and autometallography processing will be needed to control the density of Pt islands, their average diameter and the Ag shell thickness that is applied to the Pt islands via autometallography, such experimental realization is underway and will be published separately. The envisaged target for process optimization will account for as high a density as possible of core-shell islands that show gaps between them that are small enough to allow coupling.

The autometallography process to deposit Ag shells on Pt islands is needed since Pt is plasmonically inactive in the UV, visible and near IR spectral regions. On the other hand, Pt islands can be deposited by ALD in a very controlled and comparably easy to use process.\(^{26–28}\) Ag or Au or even copper can not easily directly be deposited by ALD if at all.\(^{29, 46}\) Other deposition techniques such as physical or chemical vapour deposition are not as well suited as ALD to cover highly conformally high aspect ratio surfaces such as our SiNWs and account for a very high surface to be covered with plasmonically active agents. For the sum of these reasons, it is interesting to make use of the controlled ALD deposition of plasmonically inactive Pt islands and make them plasmonically active by covering them with a thin Ag shell in a simple, self aligned autometallography process. As a result of the autometallography process the metallic Ag shell forms around the metallic Pt core of the islands as shown in Figures 2a, b. Figure 3 shows a scanning transmission electron microscopy image (STEM) of a SiNW with Pt//Ag core/shell nanoparticle structures. In the corresponding energy-dispersive X-ray (EDX) elemental mappings of the platinum Pt L\(_x\) \((\text{b})\) and the silver Ag L\(_x\) \((\text{c})\) line \((\text{c})\) clearly Pt nanoparti-
cles (violet in the map) strongly concentrated on the SiNW surface covered with Ag shell layers (cyan in the map) that correspond to the successful platinum covering with plasmonically active metallic Ag layers can be seen.

After autometallography the diameter of the core–shell island increased to almost twice the core island diameter to several tens of nanometers as shown in the TEM micrograph in Figure 2b. The thickness of the Ag shell can simply be controlled by the time of treatment in the silver lactate and hydroquinone mixture. The SERS capabilities of the Pt and Pt//Ag core–shell nanoparticles/islands on etched SiNWs with a large surface area can easily be shown by a simple model SERS experiments using dye molecules of methyl violet as the agent of interest (analyte). Figure 4 shows the results of the SERS measurements with methyl violet in a 10⁻⁵ mol L⁻¹ dilution as the analyte. SiNW substrates that were only covered with Pt islands by ALD (black curve) are compared in the aforementioned SERS experiment to SiNW substrates where the Pt nanoparticles were covered with Ag shells (cf. Figure 2) by autometallography (red curve). Due to the plasmonic activity of the Ag shells and the lack of plasmonic activity of the Pt nanoparticles/islands the following SERS results can be derived: the characteristic Raman signature of methyl violet is visible only when the dilute dye is applied to the core-shell Pt//Ag island samples but is not discernible when plasmonically inactive Pt islands alone reside on the large surface area of the etched SiNWs. In this case, only a broad carbon band is visible, indicating that sample burning occurred due to a still too high laser power on the sample.

The Raman measurements indicate that dense Pt islands on SiNWs do not lead to substantial signal enhancements, however, Ag shells on Pt islands do enhance Raman signal intensities so that characteristic Raman signatures of a highly dilute dye molecule solution can be detected. These findings are supported by FE simulations of cylindrical Pt nanocylinder dimers with increasingly thick Ag shells. Figure 5 shows the spectra of the local electric field enhancement factor for Pt//Ag core-shell cylinders. This value, which is crucial for highly sensitive Raman measurements for example, single molecule detection, is taken in the gap area of the cylindrical core–shell dimers in the center of the hot spot region. As references, pure Pt cores with no Ag shells are shown in Figure 6a with a core radius of 10 nm. The black dotted line in Figure 5 shows the electric field enhancement for a dimer consisting of pure Pt cores with 2 nm Ag shell (denoted as: Pt//Ag (10,12) the electric peak enhancement values increase with increasing Ag shell thicknesses of 2, 4, 6, 8, 10 nm, showing a slight red-shift of the resonance position. Already an Ag shell thickness of 10 nm [denoted: Pt//Ag (10,20)] shows a field enhancement factor of around 60 (corresponding to a SERS enhancement factor of ~1.3×10⁷ according to the E⁴-rule), which is close to the enhancement...
factor of pure Ag cylinders. For visualization purposes, Figure 6 shows surface plots of the electric field distribution in the calculated cylinder dimer core–shell structures. For each shell thickness the corresponding core–shell cylinder dimer is shown. The colour code is logarithmic and encodes the local electric field enhancement factor. The maximum factor of 4.1 represents a field enhancement $E_{\text{local}}/E_{\text{inc}}$ of around 60 which roughly corresponds to a SERS enhancement factor of $\sim 1.3 \times 10^5$ (according to the E^4-rule).

![Figure 6. Color coded values of the electric field enhancement factor in Pt/Ag core–shell dimers with increasing Ag shell thicknesses and constant Pt core radius of 10 nm. The logarithmic color code represents the local electric field enhancement factor. The maximum factor of 4.1 represents a field enhancement $E_{\text{local}}/E_{\text{inc}}$ of around 60 which roughly corresponds to a SERS enhancement factor of $\sim 1.3 \times 10^5$ (according to the E^4-rule).](image-url)

Acknowledgements

The authors thank Mrs. S. Hopfe (Max Planck Institute of Microstructure Physics, Halle/Germany) for TEM sample preparation. Financial support by the European Commission (FP7 program in the ROD-SOL project and FP6 program NANOSTURE) as well as the German Science Foundation (DFG, contract number CH-159/1) and the Max-Planck Society in the “Nanostress” project are gratefully acknowledged.

Keywords: atomic layer deposition · core–shell nanoparticles · SERS · silicon nanowires · surface plasmons


Received: February 11, 2010
Published online on May 5, 2010