Nanowires Enabling Signal-Enhanced Nanoscale Raman Spectroscopy

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Silicon nanowires grown by the vapor–liquid–solid (VLS) mechanism catalyzed by gold show gold caps (droplets) ≈20–500 nm in diameter with a half spherical towards almost spherical shape. These gold droplets are well suited to exploit the surface-enhanced Raman scattering (SERS) effect and could be used for tip-enhanced Raman spectroscopy (TERS). The gold droplet of a nanowire attached to an atomic force microscopy (AFM) tip could locally enhance the Raman signal and increase the spatial resolution. Used as a SERS template, an ensemble of self-organizing nanowires grown bottom up on a silicon substrate could allow highly sensitive signal-enhanced Raman spectroscopy of materials that show a characteristic Raman signature. A combination of a nanowire-based TERS probe and a nanowire-based SERS substrate promises optimized signal enhancement so that the detection of highly dilute species, even single molecules or single bacteria or DNA strands, and other soft matter is within reach. Potential applications of this novel nanowire-based SERS and TERS solution lie in the fields of biomedical and life sciences, as well as security and solid-state research such as silicon technology.

1. Introduction

Raman spectroscopy is a versatile tool that has been used for decades to perform research in a variety of different fields such as molecular chemistry, life sciences, archeology, and solid-state physics. However, the lateral resolution of conventional micro-Raman spectroscopy is limited by the diameter of the focused laser spot or in the probed sample and is usually in the range of ≈1 μm. To overcome this resolution limit, recent attempts have made use of near-field optical information during Raman measurements. As a result, the near-field scanning optical microscopy (NSOM)-Raman[1–4] or the tip-enhanced Raman spectroscopy (TERS) technique were established.[5,6] The TERS technique provides spatially selective enhancement of a Raman signal using the surface-enhanced Raman scattering (SERS) effect. The SERS effect exploits a property of nanometer-sized noble metal particles excited by incident laser photons in the form of oscillations of the surface electron charge density (plas-
mons). The plasmon-induced near field can couple, for example, with molecules or crystals in close proximity and provide an efficient pathway to transfer energy to the molecular vibrational modes and generate Raman-scattered photons that can be detected. The enhancement is maximized when the metal grains are smaller than the incident laser wavelength. The optimized particle geometry is found to be spherical or rodlike. The greatest enhancements are observed with silver, gold, and copper with grain diameters below ~200 nm. In addition to an electromagnetic-field enhancement, which is the major contribution to the SERS effect, there is an additional chemical enhancement that occurs when a molecule coordinates with the metal particle surface and forms charge-transfer states with the energy levels of the metal. This results in a charge transition usually in the visible wavelength region and a surface-localized resonance Raman enhancement. Recently, enhancement factors of $10^{20}$–$10^{14}$ have been reported with single-molecule detection of molecules absorbed on a silver substrate. The challenge is to broaden the field of applicability of Raman spectroscopy in two directions to 1) enhance the sensitivity for the detection of single molecules, bacteria, DNA, viruses, and other biological agents through optimizing the SERS effect and 2) provide for lateral resolution on the nanoscale by applying TERS.

Recently we showed that a nanowire that grows from a gold droplet that serves as catalyst for wire growth by the vapor–liquid–solid (VLS) mechanism is well suited in terms of size and shape to provide spatially selective and strong enhancement of a Raman signal exploiting the SERS effect. The challenges of implementing nanowires in TERS and of combining TERS with SERS are addressed in this Concept.

Up to now, it has been demonstrated that gold- or silver-coated atomic force microscopy (AFM) or scanning force microscopy (STM) tips show the TERS effect. However, these tips have to be coated and prior to their use the shape of the tips and their coating is usually unpredictable and rarely as sharp as a few tens of nanometers in diameter.

Our concept makes use of the self-organized growth of silicon nanowires by the VLS mechanism from a gold catalyst to serve as a TERS probe with a half-spherical-shaped Au droplet on top of the nanowire and diameters usually in the range of 15–400 nm that therefore lie within the sensitive range for field enhancement.

Our concept consists of providing a standard AFM cantilever with a solidified gold droplet on top of a silicon nanowire at the very tip. The nanowire can either be grown directly on the cantilever by in-place bottom-up VLS growth on a definite positioned gold catalyst droplet, or an existing VLS nanowire with Au droplet atop can be fixed post growth onto an AFM tip either by electron-beam-induced deposition in a SEM involving cracking of organic residual gas molecules to be used as a glue for attachment or by using a focused ion beam (FIB) machine to weld, for example, with WC or gold, materials available for deposition in these ion-beam machines. One could then use the “nanowire AFM tip” in a standard AFM, which is optically coupled with a micro-Raman spectrometer to perform TERS. With such a setup we focus on two fields of active research and technological developments, providing information that would be otherwise not accessible: 1) For applications in the biomedical field such as molecular chemistry or life sciences a combination of a nanowire-based TERS probe and a nanowire-based SERS substrate (cf. schematic image in Figure 1) could be used to maximize the enhancement and therefore improve the sensitivity of the SERS technique including the availability of spatial resolution if required. For that purpose we will establish a dimer configuration of two Au droplets between which the species of interest reside; 2) in semiconductor physics and technology the nanowire-based TERS probes could be used to: i) measure locally on the nanoscale

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**Figure 1.** a) Schematic image of a sensitive “SERS–TERS” setup that allows spatial resolution in Raman spectroscopy on the nanometer scale. The spatial resolution is obtained through the nanowire-based TERS tip. Signal enhancement is obtained when placing the material of interest on the SERS substrate, which consists of nanowire assemblies. A combination of nanowires on the SERS substrate and on the AFM tip yields a dimer configuration of gold droplets as shown in the close up (b). Strong enhancement is only achieved if the E-polarization vector (red dotted arrow) of the incident light possesses a large component along the dipole axis. With this configuration particularly strong enhancement or high detection sensitivity are envisaged.

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**Figure 2.** a) SEM data of an assembly of nanowires grown by EBE at 650 °C, 80 mA evaporation current, and a 1.2-nm sputtered Au layer on a p-type Si(111) substrate. A statistical distribution of nanowires is visible with a diameter distribution determined by the gold droplet sizes. Nanowire diameters range from 50 to 400 nm; b) SEM close up of a particularly small and a particularly large silicon nanowire next to each other. The faceted surface structure of the gold droplets on top of the large nanowire is visible.
strain/stress\(^{[17–19]}\) distributions in wafers and in nanoscale devices such as transistors, nanoscale structures such as grain boundaries in multicrystalline solar cells\(^{[20]}\) or self-organized quantum dots, or islands on misfitting substrates;\(^{[21,22]}\) ii) locally map doping profiles with nanometer-scale resolution, utilizing the Raman-specific Fano effect.\(^{[23,24]}\)

2. Silicon Nanowires: Growth and Morphology

To realize our concepts we used silicon nanowires, which were grown by electron-beam evaporation (EBE)\(^{[12,13]}\) and chemical vapor deposition (CVD)\(^{[14,15,25]}\) following the VLS growth mechanism.

2.1. EBE-Grown Nanowires

In the EBE process the nanowires grow from atomic silicon species that are generated by evaporation using an electron beam from a high-resistivity silicon target. The silicon atoms from the vapor are incorporated in the liquid AuSi eutectic alloy on the substrate surface. At supersaturation, the silicon crystallizes and the nanowires start to grow. During growth, the gold droplets stay on top of the nanowires and gold droplets form during solidification (see Figure 2). The diameter of the nanowires is determined by the size of the gold droplets, which itself depends on statistics and on the thickness of the sputtered Au starting layer.\(^{[12,13]}\) The EBE-grown nanowires used for the SERS–TERS experiments are grown within one hour at 650 °C. The growth rates lie between 20–50 nm min\(^{-1}\). For the EBE deposition of nanowires we used substrate pieces (25 mm \(\times\) 25 mm) of p-type (111) silicon wafers. Initially we deposit by sputtering a continuous Au layer on the substrate at a thickness of 0.5–3 nm. In this study we used 1.2 nm. In general, other noble metal particles are also or even better suited for SERS–TERS.
It is also possible to grow Si nanowires catalyzed by nanometer-sized Ag particles but the growth conditions are different and cannot be achieved by our growth setup. It is also possible to grow the Au-catalyzed Si nanowires and selectively deposit electrochemically Ag on top of the Au droplet. This electrochemical work is currently being explored.

The SEM micrographs in Figure 2 show an assembly of EBE-grown nanowires grown under the above-mentioned conditions by EBE (a) and two nanowires grown next to each other with one being particularly small and one being particularly large in diameter (b). The half-spherical shape of the gold droplets, well-suited for SERS and TERS,[11] is visible. The gold droplets of the small nanowire have a diameter of ∼80 nm and the diameter of the large nanowire is ∼350 nm. The length of both nanowires is about 1 μm and depends mainly on growth time; however, as expected, the thinner nanowire growing slightly faster.[12,13,26,27] The gold droplets with smaller diameters (20–150 nm) exhibit a nearly perfect smooth surface, whereas the gold droplets with larger diameters (150–500 nm) exhibit faceted surfaces with sharp edges. According to theoretical calculations,[28] gold droplets with diameters smaller than ∼150 nm produce the largest field enhancement (633-nm excitation wavelength). Often a significant SERS effect can also be generated by rather large gold droplets (see Figure 4). We assume that the facet edges at the gold droplets produce a large field enhancement in these cases.

To clarify the influence of the faceted surfaces, we also plan to systematically simulate the electromagnetic field distribution close to gold droplets within the 10–500-nm-diameter range (for the simulations the FemLab COM-SOL-Multiphysics software is used).

Depending on the direction of the E-polarization vector of the incident laser beam, we see field enhancement mainly at the following positions in the simple case of gold droplets with a smooth, nonfaceted surface:

i) E-polarization vector along the nanowire axis: At the top of a gold droplet or in between two gold droplets in case of a dimer configuration (Figure 3).

ii) E-polarization vector perpendicular to the nanowire axis: At the sides of the gold droplets close to the AuSi interface (Figure 4). Further simulations will also address the influence of the residual Si concentration contained in the Au droplets and the influence of a thin SiO₂ layer on the gold droplets.

The deep troughs around the nanowires and the pronounced faceting of the Si nanowires occur at growth temperatures above 650 °C, which were used for the growth run documented in Figure 2b. For our preliminary SERS-TERS experiments we use nanowires grown at around 650 °C or below, as shown in Figure 2a, where this trough formation around the nanowires in the Si(111) substrate is by far less pronounced. This may be of importance in order to avoid trapping of molecules (the species of interest for spectroscopic analysis) in these troughs.

2.2. CVD-Grown Nanowires

In case of the CVD experiments[14,15,25] the nanowires grow on Si(111) substrates. Prior to the deposition of a 1-nm-thick Au layer by electron-beam evaporation, the wafers were cleaned by HF and RCA. The samples were then immediately transferred into the reaction chamber, where the substrates were annealed at ∼580 °C for 10 min. This led to the formation of Au droplets with a size of between 50 and 200 nm. The temperature was then reduced to 500 °C and a mixture of Ar and SiH₄ was introduced in order to grow the nanowires for 20 min.

Figure 5 shows an example of nanowires grown by CVD. The gold droplets atop the silicon nanowires exhibit usually smaller average diameters (∼15–50 nm) than for EBE-grown wires and the size distribution of the gold droplets is narrower than in the case of EBE (see Figure 2). In addition, the gold droplets atop CVD-grown Si nanowires are more spherical rather than half spheres.
3. Silicon Nanowire Assemblies as SERS Substrates

The SERS and TERS capabilities of the Si nanowires with the gold droplets on top can easily be shown by SERS experiments. In our case, we perform micro-Raman measurements on templates that consist of nanowire assemblies from EBE and CVD experiments, which are coated with a molecular layer of malachite green or adenine molecules. To achieve such a molecular coverage of dye or biomolecules, the templates are rinsed in an aqueous solution of malachite green ($10^{-3}$ mol L$^{-1}$) or adenine ($10^{-4}$ mol L$^{-1}$) and are subsequently rinsed in deionized water. For the micro-Raman measurements we use a Jobin Yvon Labram HR 800 spectrometer equipped with a HeNe laser (633 nm) and an Ar ion laser (488 nm and 514 nm), operated with the HeNe laser for the SERS measurements. The unamped laser power on the sample surface is $\approx 10$ mW. The laser is focused by a 100x objective lens (numerical aperture: 0.9) to an effective spot size of $\approx 1$-m diameter. To reduce photobleaching, the laser intensity is damped by a factor of 10 (adenine) to 100 (malachite green) with a grey filter. That is, the energy density within the focused laser spot is $\approx 6 \times 10^4$ W cm$^{-2}$ (adenine) to $6 \times 10^3$ W cm$^{-2}$ (malachite green). Using a motorized $x$–$y$ stage we are able to perform SERS mappings and can determine SERS-active regions within the nanowire assembly.

A typical nanowire assembly to serve as a SERS substrate (grown by EBE) for the SERS mappings is shown in the SEM micrograph in Figure 2a, where nanowires with gold-droplet diameters within the range of about 50–400 nm are visible.

The optical micrograph in Figure 6a shows a top view of a nanowire assembly (grown by EBE), which is used for the SERS mapping in Figure 6b. The mapped area is indicated by the red rectangle. The gold droplets with diameters of $\approx 200$–400 nm on top of the nanowires are just discernible as blurred white spots in the optical micrograph. In Figure 6b a mapping of the intensity of the 1618 cm$^{-1}$ (in-phase stretching of the phenyl ring$^{[28,29]}$) band of malachite green is shown. A large SERS effect occurs at positions where two or three gold droplets of nanowires are close to one another and form a cluster of nanowires. This type of nanowire cluster is indicated by red dotted arrows. The spectra recorded at three positions on the nanowire SERS template are shown in Figure 6c. The spectra recorded at the indicated nanowire cluster (red and green spectra) show a significant SERS effect. Regions without any nanowires show the broad fluorescence band of malachite green and only a very faint, if any, Raman signal (blue spectrum in Figure 6c).

Though the nanowire cluster regions produce the largest SERS signal, a single gold droplet atop a nanowire is also capable of generating a significant SERS signal. This is of great importance as we intend to use a single nanowire gold droplet as a TERS probe (see next section). An example is given in Figure 7. The light optical micrograph in Figure 7a shows the top view of a single gold droplet atop a nanowire with a diameter of $\approx 200$ nm, which is just discernible as a blurred whitish spot. The red spectrum shown in Figure 7b was acquired with the centre of the focused laser spot ($\approx 1$-m diameter) on the single gold droplet. The blue spectrum corresponds to a measurement position on the bare substrate close to the single nanowire gold droplet. Regarding these two spectra it is evident that even a single nanowire gold droplet produces a remarkable SERS signal.

The optical micrograph in Figure 8a shows a top view of a nanowire assembly grown by CVD, which is used for the SERS mapping of adenine molecules shown in Figure 8c. The mapped area is again indicated by the red rectangle. The gold droplets with diameters of now $\approx 40$–80 nm on top of the nanowires are no longer discernible in the optical micrograph. We used the substrates grown by CVD as these nanowire gold droplets produce, in the case of adenine molecules, much stronger SERS signals than the EBE-grown nanowire gold droplets. The large difference in SERS signal intensity does not occur in the case of malachite green. The reasons for the different molecule-dependent SERS sensitivities are not yet fully understood and need further investigation. Figure 8b shows a mapping of the intensity of the $\approx 1370$ cm$^{-1}$ band of the adenine molecule. A large SERS effect occurs at this position, which is indicated by the red arrow. A hot spot (red area in the Raman mapping) might reside at this position. The green regions show moderate SERS signals and within the
blue regions the SERS signal is too weak to show distinct bands of the adenine molecules.

4. Nanowire-Based TERS Probe

A nanowire-based TERS probe can in principle be produced in two different ways: a) A silicon nanowire with a gold droplet atop can be grown directly on, for example, a silicon AFM cantilever by the growth method described in Section 2. This requires the precise in-place positioning of a Au droplet on the AFM cantilever to catalyze subsequent bottom-up nanowire growth; b) a silicon nanowire can be welded onto an AFM tip. One method to do so is the electron-beam-induced contamination deposition. This method was used for the example shown in Figure 9. Other options are to use an FIB machine for welding or focused electron beam (FEB)-induced deposition of, for example, WC, gold, platinum, or other materials.[30]

For our concept we used method (b) (preliminary results with method (a) have been obtained but are not shown here[31]). The fabrication of a nanowire-based TERS probe by method (b) needs in general three steps, which are shown in the sequence of the SEM images in Figure 9a–f.

i) At first, a large number of silicon nanowires have to be broken off the substrate using a moving AFM tip as a kind of lawn mower for nanowires. The removed nanowires either fall away into the vacuum, onto the substrate, or onto other nanowires.

ii) With a nanomanipulation setup inside an SEM,[32] a nanowire of acceptable shape and diameter can be chosen and aligned with the AFM tip.

iii) The aligned nanowire can be attached to the AFM tip by electron-beam-induced deposition of carbonaceous contaminants present on the sample surface and in the residual gas of the SEM chamber. Applied to a large enough area around the joint, this deposit is stronger than either the nanowire itself or the AFM tip.

So far, we have not performed any systematic Raman measurements with the nanowire-based TERS probes. However, the preliminary results of the measurements shown in Figures 6 and 7 are promising and show that the nanowire-based TERS probe and the nanowire-based combined TERS/SERS setup are capable of producing a large SERS signal with a spatial resolution on the nanometer scale.

5. Conclusions and Outlook

Silicon nanowires grown by the VLS mechanism in an EBE or CVD reactor from a gold catalyst show gold droplets on top with either a nearly half-spherical (EBE VLS nanowire growth) or nearly complete spherical shape (CVD VLS nanowire growth), which can be used to exploit the tip- or surface-enhanced Raman effects. When a nanowire with a gold droplet is attached to an AFM tip the signal enhancement by the gold droplet can be used to spatially resolve a Raman signal on the nanometer scale, that is, to perform nano-Raman spectroscopy in a suitable optically coupled combined AFM/Raman setup.

A combination of a nanowire-based TERS probe and a nanowire-based SERS substrate promises optimized field enhancement that could be used for the detection of single molecules, DNA strands, bacteria, and other soft matter. Potential applications of this novel nanowire-based technical SERS and TERS solution are widespread and lie in the fields of biomedical and life science as well as security and solid-state research such as in silicon technology, where the detection of materials composition, doping, and lattice strain can be probed by Raman spectroscopy, using TERS with the spatial resolution of the nanowire-based AFM tip.
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References


Figure 9. Nanomanipulation sequence for the attachment of an upside-down nanowire onto an AFM tip; a) some nanowires are broken off the substrate mechanically by the movement of an AFM tip; b) a nanowire that lies on the substrate surface is brought into contact with the AFM tip; c) the nanowire is moved into the desired position; d) welding of the nanowire to the AFM tip by electron-beam-induced contamination; e) retraction of the AFM tip; f) cantilever with tip and welded nanowire assembly to be used as a TERS probe.