Signal enhancement in nano-Raman spectroscopy by gold caps on silicon nanowires obtained by vapour–liquid–solid growth

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Abstract

Silicon nanowires grown by the vapour–liquid–solid growth mechanism with gold as the catalyst show gold caps \(\sim 50–400\) nm in diameter with an almost ideal hemispherical shape atop a silicon column. These gold caps are extremely well suited for exploiting the tip or surface enhanced Raman scattering effects since they assume the right size on the nanometre scale and a reproducible, almost ideal hemispherical shape. On attaching a nanowire with a gold cap to an atomic force microscopy (AFM) tip, the signal enhancement by the gold nanoparticle can be used to spatially resolve a Raman signal. Applications of this novel nanowire based technical tip enhanced Raman scattering solution are widespread and lie in the fields of biomedical and life sciences as well as security (e.g. detection of bacteria and explosives) and in the field of solid state research, e.g. in silicon technology where the material composition, doping, crystal orientation and lattice strain can be probed by Raman spectroscopy. A prerequisite for obtaining this spatial resolution in nano-Raman spectroscopy is the attachment of a nanowire with a gold cap to an AFM tip. This attachment by welding a nanowire in a scanning electron microscope to an AFM tip is demonstrated in this paper.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Raman spectroscopy is a versatile tool in use for decades for performing materials research in a variety of different fields, such as molecular chemistry, life sciences, archaeology, and solid state physics. However, the lateral resolution of conventional micro-Raman spectroscopy is limited by the diameter of the focused laser spot on or in the probed sample and is usually at best in the range of \(\sim 1\) \(\mu\)m. To overcome this resolution limit, recently attempts were made to make use of near field optical information during Raman spectroscopy. As a result the near field scanning optical microscopy (NSOM) Raman or the so-called tip enhanced Raman spectroscopy (TERS) technique arose \cite{1–4}. The TERS technique provides spatially selective enhancement of a Raman signal using the surface enhanced Raman scattering (SERS) effect \cite{4, 5}. The SERS effect exploits a property of nanometre sized metal particles or surface grains and relies on the geometry of the metal particles \cite{6–8}. Incident laser photons are absorbed into the metal particles through oscillations of surface electron...
charge density (plasmons). The plasmon radiation can couple e.g.
with molecules or crystals in close proximity and provide
an efficient pathway by which to transfer energy to their
vibrational modes, and generate Raman photons that can be
detected. The Raman signal enhancement is maximized when
the metal grains are smaller than the incident laser wavelength,
the metal has the optical properties to generate surface
plasmons and an optimized geometry of the metal nanograins
is available [9]. The greatest enhancements are observed
with silver, gold, and copper with grain diameters between
10 and 200 nm [6, 7]. In addition to an electromagnetic
field enhancement, that contributes the majority to the signal
enhancement, 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 transfer transition in the
visible wavelength region and a surface localized resonance
Raman enhancement. Recently, enhancement factors of $10^{13}$–
$10^{14}$ have been reported with single-molecule detection of
molecules absorbed on a silver substrate [8, 10]. The challenge
is to broaden the field of applicability of Raman spectroscopy
in two directions:

(i) enhance the sensitivity for the detection of single
molecules (e.g. of gas or explosives), bacteria, DNA
strands, viruses and other biological agents through
optimizing the SERS effect and

(ii) provide for lateral resolution on the nanometre scale
through the application of TERS.

How to address these challenges is discussed in this paper and
**nanowire** based solutions are shown.

Already it has been demonstrated [4, 5] 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 metal coated prior to their use; the shape of the
tips is unpredictable and not reproducible and rarely as sharp
as a few tens of nm in diameter.

Our concept makes use of the self-organized growth of
silicon nanowires by the VLS mechanism [11–14] from gold
catalyst to serve as a TERS probe, when attached to an AFM
cantilever, with an ideal hemispherically shaped gold cap at the
tip of the nanowire and diameters usually in the range of 50–
400 nm so that the smaller nanowire gold caps lie within the
sensitive range for field enhancement [6, 7].

We will show in this paper that we can provide a modified
standard AFM cantilever with a solidified gold cap of a silicon
nanowire at the very tip that could be used as a TERS probe.

In principle, either the nanowire can be grown directly on the
cantilever by in-place, bottom-up VLS growth on a positioned
gold catalyst particle, or, and this is the method we
will show in this paper, assemblies of nanowires can be grown
by the VLS mechanism on a substrate and can be chopped off from there and welded ‘post-growth’ onto an AFM tip, e.g.
using an electron beam in a scanning electron microscope
(SEM) to weld carbon species with natural residues within
the SEM (used in this paper) or using a focused ion beam (FIB)
machine to weld e.g. with WC$_3$ or platinum 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 set-up the incident laser beam is focused
onto the region close to the gold cap on the silicon nanowire,
where the field enhancement is realized.

In order to prove the SERS capability of nanowires we use
a well-studied model substance, malachite green, that shows
a characteristic, prominent Raman spectrum. A molecular
coverage of nanowires with malachite green is realized and
enhanced Raman signatures are detected. To prove the TERS
capability of gold caps atop silicon nanowires, the Raman
signal enhancement produced by a single gold cap is measured.

2. Results

2.1. Silicon nanowires: growth and morphology

To realize SERS and TERS with silicon nanowires with
gold caps we grew nanowires by electron beam evaporation
(EBE) [13, 14] using the VLS growth mechanism. In EBE
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 vapour
are incorporated in the liquid Au–Si eutectic alloy on the substrate.
At supersaturation, the silicon crystallizes and the
nanowires start to grow. During growth, the gold caps stay on
top of the nanowires and during solidification, almost perfect
hemispherical gold caps form. The diameter of the nanowires
is determined by the size of the gold cap which itself depends
on statistics and on the thickness of the sputtered gold starting
layer. For the EBE deposition of nanowires we used substrate
pieces (25 mm × 25 mm) of p-type (111) silicon wafers.
Initially, we deposited by sputtering a continuous gold layer
on the substrate at a thickness of e.g. 0.5–3 nm. This gold
layer disintegrates upon annealing at the growth temperature
into gold droplets, distributed in size with an average diameter
of the order of a few tens of nanometres. These gold droplets
are statistically distributed on the substrate surface and catalyse
the one-dimensional nanowire growth [11–16].

The scanning electron microscopy (SEM) micrograph in
figure 1 shows an assembly of nanowires. The almost ideal (for
SERS and TERS [6]) hemispherical shape of the gold caps atop
the Si columns underneath is visible. The gold hemisphere on
Si columns (nanowires) is for SERS and TERS geometrically

![Figure 1. SEM micrograph of an assembly of Si nanowires grown by EBE at 700 °C heater temperature on a p-Si(111) substrate. A statistical distribution of nanowires is visible with a diameter distribution determined by the gold cap sizes. Nanowire diameters range from 50 to 400 nm.](image-url)

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Figure 2. SEM micrograph of an assembly of nanowires (right side of the micrograph) grown by EBE in this case at 700 °C heater temperature, on a p-Si(111) substrate and lens shaped gold (Au) droplets (left side of the micrograph) under the substrate holder clamp so that the evaporated silicon did not reach there, but heating to the growth temperature occurred so as to disintegrate the continuous gold layer into lens shaped gold droplets.

preferred compared to the essentially lens shaped gold droplets that form upon annealing of the continuous gold layer on the silicon substrate, prior to nanowire growth. The difference between gold droplet shape (gold caps) on nanowires and on the bare substrate surface is visible at the rim of the sample, under the substrate holder clamp (cf figure 2). The length of the nanowires varies and depends mainly on growth time, however, with the thinner nanowires growing a little faster, just as expected [13–16].

2.2. Silicon nanowire assemblies as SERS substrates

The SERS and TERS capabilities of the Si nanowires with the gold caps atop can easily be shown by simple SERS experiments. In order to prove the SERS capability of gold caps atop nanowires, we use a well-studied model substance, malachite green, that shows a characteristic Raman spectrum. A molecular coverage of nanowires with malachite green is realized dipping the sample with nanowires in an aqueous solution of malachite green and subsequently rinsing the sample in de-ionized water. The Raman measurements were carried out in areas with nanowires and between nanowires on the bare silicon substrate (with the molecular coverage of malachite green). The Raman mappings were carried out with a Jobin Yvon LabRam HR800 spectrometer. For excitation the 633 nm emission line of a HeNe Laser was used. The undamped laser power on the sample was ~10 mW. To avoid degradation of molecules due to heating, the laser power was damped by a factor of 100 with a grey filter. With a 100× objective lens (numerical aperture: 0.9) the focused laser spot on the sample surface was ~1 µm in diameter, i.e. the resulting energy density within the spot was ~1.3 × 10^4 W cm⁻². All measurements were carried out using the z’une scattering geometry. That is, 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.

The gold caps of diameters between ~100–400 nm on top of the nanowires are just discernible as blurred whitish spots in the dark areas (that dark areas originate from troughs around the nanowires) in a light optical microscope if the 100× objective lens is used. Figure 3 shows an optical micrograph with three regions indicated by (a), (b), (c) where Raman intensities of malachite green [17, 18] between 1000 and 1800 cm⁻¹ were recorded. The nanowire density of the sample used for these measurements is lower than the nanowire densities of the samples shown in figures 1 and 2. Using this sample, we were able to perform Raman measurements at positions were only a few (2–3; spectra (a) and (b) in figure 3) nanowires, a single nanowire (see figure 4) or no nanowires resident (spectrum (c) in figure 3). The spectrum (c) in figure 3 shows the broad fluorescence band of malachite green and essentially no Raman signal ((c), blue spectrum). The coloured circles in the light optical micrograph represent the diameter of the focused laser spot.

2.3. The nanowire based TERS probe

After having proven the SERS capability of gold capped nanowires, a nanowire based TERS probe is produced by welding a silicon nanowire with a gold cap onto an
Figure 4. The inset shows the light optical micrograph of a single nanowire gold cap with a diameter of \(\sim 300\) nm. The Raman spectra recorded at the positions indicated at the single gold cap (red, a) and close to the gold cap on the bare substrate surface (blue, b) are shown. The circle represents the size of the focused laser spot. The spectrum shows that even a single nanowire gold cap with even a somewhat larger diameter is capable of producing a significant signal enhancement. Consequently, the gold caps atop silicon nanowires can be assumed to be well suited to be used as TERS probes.

AFM tip using the electron beam induced contamination deposition [19]. The fabrication of a nanowire based TERS probe needs in general three steps, which are shown in figure 5:

(i) At first, a large number of Si nanowires have to be chopped off the nanowire substrate using a moving AFM tip as a kind of 'lawnmower' for nanowires. The broken nanowires fall either somewhere onto the Si substrate or less often onto other nanowires or they are sucked away by the pumping system of the scanning electron microscope (SEM).

(ii) With a nanomanipulation set-up inside an SEM [20], a geometrically, suitable for SERS and TERS, nanowire can be chosen and can be 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 surfaces and in the residual gas of the SEM chamber. Applied to a large enough area around the joint, this deposit can be stronger than the nanowire itself or the AFM tip [21].

Up to now, the nanowire based TERS probe has not been systematically tested in a TERS set-up as the necessary experimental set-up (optically coupled Raman spectrometer and AFM) is still under construction. However, the Raman signal can be enhanced by single gold caps, as shown in figure 4. This finding promises that nanowire based TERS probes will show Raman signal enhancement with spatial resolution on the nanometre scale.

2.4. The nanowire based TERS probe for an enhanced Raman effect with spatial resolution on the nanometre scale

Especially for today’s applications in solid state physics and technology it is of utmost importance to have spectroscopic Raman capabilities with a probe size of the nanometre scale. Focusing the exciting laser on the surface gives, however, at best, probing spots of the order of \(\sim 1\) \(\mu m\) depending on the specifics of the set-up (laser, wavelength, focusing optics, gratings, a.o.). Using the nanowire based TERS probe, anticipating enhancement under the tip to be sufficiently high for distinguishing a Raman signal from the entire probed volume and the volume under the TERS tip, it would be possible to get spectroscopic information with the resolution determined by the dimensions of the TERS tip. Taking a look at our experimentally realized nanowire based TERS tip, shown in figures 5 and 6, we can state the following: the tip as is has a gold cap with a diameter given by the nanowire diameter.
distributions [23, 24] or train [25] that is utilized in present is too large for spatially resolving and measuring e.g. implant grown by chemical vapour deposition, e.g. [29, 30], with high mechanical strength at diameters of 20–40 nm [20]. This type with gold caps is currently under way.

Figure 6. (a) SEM micrograph of a nanowire based TERS probe, i.e. a nanowire with a gold cap atop welded by a focused electron beam to a commercially available AFM tip using carboaceous species in the residual gas of an SEM; (b) close-up of the silicon nanowire with a gold cap at the very tip; (c) transistor of the 90 nm technology node downloaded from the Intel Web site [26] for direct comparison (reproduced by permission from Intel); (d) nanowire grown by chemical vapour deposition as described in [29, 30] with diameters ranging from 20 to 40 nm.

We could up to now realize diameters of the gold caps of ∼50–400 nm (figures 5 and 6). For today’s transistors of the 90 nm technology node [22] as shown in a cross-sectional transmission electron micrograph in figure 6(c), this type of tip is too large for spatially resolving and measuring e.g. implant distributions [23, 24] or strain [25] that is utilized in present and future transistor generations [26–28] and that requires quality control based on strain determination on the nanometre scale where up to now no satisfactory method has been identified. With our nanowire based TERS probe, in principle, this problem can be attacked. For that purpose, however, we still need to realize the welding of thinner nanowires (an example is shown in figure 6(d)) that for example can be grown by chemical vapour deposition, e.g. [29, 30], with high mechanical strength at diameters of 20–40 nm [20]. This type of TERS probe realization by welding of thinner nanowires with gold caps is currently under way.

3. Conclusions

Silicon nanowires grown by the vapour–liquid–solid mechanism catalysed by gold show gold caps atop a silicon column with an almost ideal hemispherical shape to be used to exploit the tip or surface enhanced Raman (TERS/SERS) effects. Attaching a nanowire with a gold cap at an AFM tip, the Raman signal enhancement by the gold cap can be used to spatially resolve a Raman signal on the nanometre scale, i.e. to perform nano-Raman spectroscopy.

Applications of this novel nanowire based SERS and/or TERS measurement arrangement are widespread and lie in the field of biomedical and life sciences as well as security and in the field of solid state research, e.g. in silicon technology where material composition, doping, and lattice strain can be probed by Raman spectroscopy, now using TERS with the spatial resolution of the nanowire based AFM tip.

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References

[3] Sun W X and Chen Z X 2003 J. Raman Spectrosc. 34 668
[18] Doering W E and Nie S M 2003 Anal. Chem. 75 6171
[22] International Technology Roadmap for Semiconductors http://public.itrs.net/