# **PROCEEDINGS OF SPIE**

SPIEDigitalLibrary.org/conference-proceedings-of-spie

# Potential application of tip-enhanced Raman spectroscopy (TERS) in semiconductor manufacturing

P. Y. Hung, Thomas E. O'Loughlin, Aaron Lewis, Rimma Dechter, Martin Samayoa, et al.

P. Y. Hung, Thomas E. O'Loughlin, Aaron Lewis, Rimma Dechter, Martin Samayoa, Sarbajit Banerjee, Erin L. Wood, Angela R. Hight Walker, "Potential application of tip-enhanced Raman spectroscopy (TERS) in semiconductor manufacturing," Proc. SPIE 9424, Metrology, Inspection, and Process Control for Microlithography XXIX, 94241S (19 March 2015); doi: 10.1117/12.2175623



Event: SPIE Advanced Lithography, 2015, San Jose, California, United States

# Potential Application of Tip-Enhanced Raman Spectroscopy (TERS) in Semiconductor Manufacturing

P.Y. Hung<sup>a</sup>, Thomas E. O'Loughlin<sup>b</sup>, <sup>d</sup>Aaron Lewis, <sup>d</sup>Rimma Dechter, Martin Samayoa<sup>a</sup>, Sarbajit Banerjee<sup>b</sup>, Erin L. Wood<sup>c</sup>, and Angela R. Hight Walker<sup>c</sup>

<sup>a</sup>SEMATECH, Albany, NY, 12203, USA

<sup>b</sup>Texas A&M University, College Station, TX 77842

<sup>c</sup>Semiconductor and Dimensional Metrology Division, NIST, Gaithersburg, MD 20899

<sup>d</sup>Nanonics Imaging Ltd., Jerusalem, Israel

#### Abstract

Tip-enhanced Raman spectroscopy (TERS), with nanometer spatial resolution, has the capability to monitor chemical composition, strain, and activated dopants and is a promising metrology tool to aid the semiconductor R&D processes. This paper addresses the major challenges which limit the application of TERS from routine measurement: the lack of comparability, reproducibility, calibration, and standardization. To address these issues, we have developed a robust test structure and the ability to generate high-quality tips using a high volume manufacturing (HVM) approach. The qualifying data will be presented.

Subject Terms: Tip enhanced Raman spectroscopy, TERS, defect metrology, strained Si

#### 1. Introduction

The 2012 ITRS roadmap forecasts that the physical dimensions of device components will scale down to 10 nm as early as 2020. To achieve this goal, it is imperative to have relevant metrology (preferably amenable to large-scale in-line deployment) to monitor chemical composition, strain and activated dopants with nanometer spatial resolution. The techniques currently used are either destructive, require extensive sample preparation, are very difficult to tailor for *operando* measurements (for instance, transmission electron microscopy [TEM]), or are limited in their ability to deliver required information such as chemical composition and bonding (atomic force microscopy [AFM]).

Tip-enhanced Raman spectroscopy [TERS] is a promising technique that is well suited to fill the abovementioned existing metrology gap. It combines the benefits of AFM nanometer-scale resolution with the Raman capability to monitor chemical composition, density of activated carriers (through phonon-plasmon coupled features), and lattice strain. The measurements can be performed in ambient environments with little or no sample preparation.

This work addresses the major challenges that limit the application of TERS for routine measurements: the lack of comparability, reproducibility, calibration, and standardization. It also explores the potential application of TERS for defect metrology and device monitoring. To address these challenges, we have developed a robust test structure and the ability to generate high-quality tips using high volume manufacturing (HVM) approaches. Illustrative examples of plasmonic enhancement demonstrate that our gold tip template generates sufficient signal for the detection of sub-30 nm polystyrene particles and sub-10 nm  $HfO_2$  nanorods.

Metrology, Inspection, and Process Control for Microlithography XXIX, edited by Jason P. Cain, Martha I. Sanchez, Proc. of SPIE Vol. 9424, 94241S · © 2015 SPIE CCC code: 0277-786X/15/\$18 · doi: 10.1117/12.2175623

### 2. DESIGN AND EVALUATION OF TEST STRUCTURE

To address a critical gap in the standardization of TERS measurements, a test structure has been designed that is directly relevant to the semiconductor community and enables the evaluation of spatial resolution and signal enhancement for TERS measurements [1]. Additional applications of the test structure include establishing a performance baseline for the tool, troubleshooting tool issues, and optimizing measurement conditions. When combined, these applications enable comparability and validation across laboratories and for daily tool monitoring as well.

Previously, Saito et al., [2], Zhu et al., [3], Hecker et al., [4], and Okuno et al., [5] demonstrated semiconductor-suitable test structures using strained silicon-on-insulator (SOI) and SiGe. This work uses SiGe, which is more readily available than strained SOI. In particular, we use our SiGe FinFET process flow (25% Ge) which generates a repeated SiGe line pattern with line width from sub 40 nm up to 7500 nm. This mass production approach ensures that the test structure has the physical dimensions relevant to the semiconductor manufacturing industry.

Figures 1a to 1c show the top-down SEM and the cross section TEM images of the FINFET test structure. The SiGe lines are much wider at the bottom. An etching process was used to expose the narrow top portion of the lines and the line width as measured through TEM is used for evaluating the spatial resolution of TERS. Figure 2 outlines the etch process together with a schematic of the test structure.







Figure 2 TEM cross-section of a single SiGe line with etch-away area highlighted in yellow (left). Schematics of a postetched test structure with the top uniform portion of the SiGe lines exposed (right). The test structures were evaluated with a Nanonics MV-4000 scanning probe microscope (SPM) in a single probe configuration, coupled to a Renishaw inVia Raman microscope (Figure 3a). The Nanonics system is equipped with two flat piezo scanners with a completely open optical axis, which enables the seamless integration of an AFM probe in 180° Raman back-scattering configuration (Figure 3b). There are three important design aspects to enable semiconductor material characterization using this TERS system. The first is the ultrathin scanner (7 mm) which allows for optical access from above (Figure 3b). The second is a tuning fork AFM feedback system (Figure 4) instead of a conventional sensing laser set up. The tuning fork feedback has a force sensitivity up to 1.6 pN without jump-to contact instabilities [6] and also eliminates interference between the sensing laser and Raman excitation laser. The third distinctive feature is the use of glass probes which to avoid blocking of the Raman laser beam. A gold particle was secured at the open end of the glass tip (Figures 4 & 5) to generate local plasmonic enhancement [7].



Note: SPM allows optical access from top or bottom of the scanners.

Figure 3 a) Nanonics MV-4000 SPM system\* coupled to a Renishaw Raman microscope and b) SPM Setup.

\*Certain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.



Note: Cantilevered probes with exposed apex mounted on the tuning fork provides optimal geometry for optical integration.

Figure 4 Tuning fork AFM feedback system.



Figure 5 Glass Probe with gold particle tip for TERS measurement

To evaluate the TERS signal enhancement, we compare the Raman signal intensity collected when the TERS probe is in contact with the sample (probe in) and when the TERS probe is placed ~ 1  $\mu$ m above the sample and does not contact the sample (probe out). Here, we select the strained Si Raman signal at ~ 510 cm<sup>-1</sup> for evaluation; the measurements were independently taken at both Nanonics' headquarters and NIST using two test structures generated from the same process flow. Figures 6a and 6b are spectra collected from Nanonics and NIST, respectively. When the gold particle probe is in contact with the test structure (probe in), the substrate Si signal has little or no enhancement whereas the strained silicon signal is enhanced.



Figure 6 Tip enhanced Raman spectra collected from SiGe test standards using probe in and probe out condition a) data collected in Nanonics Headquarter and b) data collected by NIST.

The enhancement factor was calculated using Eq. [1], with the caveat that different equations can be used and a uniform consensus is yet to emerge regarding a definitive mode of calculating enhancement [8]:

TERS enhancement factor 
$$= \frac{I_{ters}}{I_{far}} * \frac{V_{far}}{V_{ters}}$$
[1] Eq. [1]

Where:

- $I_{ters}$  and  $I_{far}$  are the raw intensities of the Raman strained Si peak at 510 cm<sup>-1</sup> with the TERS tip in contact (I <sub>TERS</sub>) and in the far-field, or probe out (I<sub>Far</sub>)
- $V_{ters}$  and  $V_{far}$  are the volumes from which the Raman signals originate. The  $V_{ters}$  value is based on the nano-plasmonic properties of the gold particle [8].
- $V_{far}$  is based on the diffraction limit of 532 nm excitation for Nanonics and 514 nm for NIST.

Nanonics reported an enhancement factor of 8999 and NIST reported a slightly lower value of 7108. Both results are in the range of 1E+04 which falls within the published values [3]. This result indicates that the FinFET process can mass produce test structures with good fidelity and also shows the potential application of the test structure for tool performance comparison.

The spatial resolution measurement was performed at Nanonics headquarters using TERS mapping. As with the comparison of signal intensity, we focused on the strained Si signal at  $\sim$ 510 cm<sup>-1</sup> (from SiGe) and compared the TERS maps between "probe in" and "probe out" set up. In the "probe in" condition (Figure 7 - upper left) we are able to resolve the individual lines of the SiGe line. On the contrary, using the "probe out" set up (Figure 7 - upper right), we can only detect the presence of strained Si, but are unable to resolve the line pattern. The TERS line scan (Figure 7 - lower left) shows line width of 40 nm, which is at least 10 nm wider than our TEM result (Figure 8).



Figure 7 TERS and micro-Raman imaging for 510 cm<sup>-1</sup> (strained Si).



Figure 8 TEM cross-section taken from the narrowest SiGe area in our test structure showing pitch at  $\sim$  209 nm (left) and TEM image showing SiGe line width at 24 nm with height at 6.72 nm (right).

# 3. OPTIMIZE PROCESS TO GENERATE REPRODUCIBLE TERS TIPS

Chemical imaging with a spatial resolution of a few tens of nanometers is achievable by plasmonic enhancement in TERS imaging, but has thus far been plagued by the lack of reproducible manufacturing processes for fabrication of high-quality tips. Our goal is to establish a pilot process to generate a template with dense array of gold for coating AFM tips. Such a template can generate cost effective and repeatable tips and give the TERS user the flexibility to coat a tip immediately before measurement. The last benefit is especially important for less stable coatings such as silver. We leveraged on a pilot process originally proposed by Johnson et al.,[9] (Figure 9) and optimized it by adding an electrochemical etching for step 5. Figures 10–12 show our results from various processing steps. In comparison to a non-electrochemical procedure, our approach is much more efficient and yields a cleaner etch surface (Figure 14). Figure 13 depicts the electrochemical etching apparatus developed in our laboratories, wherein a copper plate is used as a backstop and to support silicon templates. A Pt wire was used as the cathode with the silicon template functioning as the working electrode. The Si substrate was etched via the following balanced equations:

Anodic reaction: Si (s) + 6F<sup>-</sup>(aq.) + 2H<sup>+</sup>(aq.) + 2h<sup>+</sup>  $\rightarrow$  SiF<sub>6</sub><sup>-2-</sup>(aq) + H<sub>2(g)</sub>

Cathodic reaction:  $2H^+(aq) + 2e^- \rightarrow H_2(g)$ 

Overall etching reaction: Si (s) + 4H<sup>+</sup> (aq.) + 6F<sup>-</sup> (aq.)  $\rightarrow$  SiF<sub>6</sub><sup>2-</sup> (aq.) + 2H<sub>2</sub> (g)

Using this electrochemical etch, we achieved a greater than 90% yield. Figure 15b shows a lowmagnification, top-down SEM image of our template. The bright spots are gold pyramids that remain intact and the dark spots are pyramids that have fallen out from the template and are not available for AFM tip coating. There are about 700 pyramids shown; less than 20 fell out (i.e., 3% failure rate). Figure 15c is a high-magnification, top-down SEM image from our gold-plated template indicating the high quality of the template.



Note: Idea based on Johnson et al.[9]

Figure 9 Process Flow for making a TERS tip template.



Figure 10 a) Top-down SEM image and b) Cross-section SEM image showing patterned photoresist with exposed Si primed for KOH Etch.



Figure 11 a) Post KOH etch silicon template and b) After a 30 min sonication in isopropyl alcohol.



Figure 12 Low resolution top down SEM image gold coated template (left) . Magnified image of a single inverted gold pyramid(left).



Figure 13 a) Image of the HF etching setup used and b) cutaway diagram of setup.



Figure 14 SEM images of undamaged gold pyramids after HF etching for 5 min( top left), electrochemical HF etching yield a cleaner gold pyramid and takes only 2 min (top right).



Figure 15 Finished array of "gold pyramids". a) High resolution SEM image for a gold pyramid . b) Low magnification top-down SEM of template. The bright dots in the repeated array are intact gold pyramids. The dark spots are slots where the gold coating was delaminated and removed during the etching process ;c) high magnification top-down SEM image of a finished template reveals the high quality of gold pyramids' array.

A technique for binding gold pyramids to the AFM tip using poly(dimethylsiloxane) (PDMS) as an adhesive is being developed. PDMS was chosen due to the slow curing time and flexibility to adjust viscosity by tuning the curing temperature. In ongoing work, we will place the PDMS on the template in close proximity to the gold pyramids. After picking up the PDMS, we will align the AFM tip to a gold pyramid and adhere the gold pyramid to the tip as illustrated in Figure 16.



Figure 16 Experimental setup where a binding agent PDMS is placed in close proximity to gold pyramids on a template. We first pick up small amount of PDMS on the AFM tip, then align the tip to pick up a gold shaped pyramid from the template .

## 4. EVALUATION OF THE POTENTIAL OF TERS FOR NANOSCALE MONITORING

We have devised a simple test to verify the plasmonic signal enhancement from our fabricated gold pyramids. Specifically, by placing analytes inside the gold pyramids to determine if the Raman signal from the analytes is enhanced by plasmonic effects. We used 30 nm diameter polystyrene latex (PSL) particle and  $HfO_2$  nanorods to test the signal enhancement. Neither material has sufficient signal from conventional micro Raman.

PSL was used to mimic the presence of carbonaceous species such as photoresists or airborne contamination—which pose challenges in defect monitoring. As CMOS scaling continues, there is an imminent need to monitor and identify defects down to sub-30 nm dimensions. Currently, defect characterization is routinely performed by energy dispersive X-ray spectroscopy (EDS). EDS is inefficient in monitoring sub-30 nm defects. Furthermore, EDS only provides elemental information, and thus cannot provide precise identification of carbonaceous species. A clear Raman signal from 30 nm PSL using our template indicates that TERS is likely to have sufficient signal amplification and therefore sensitivity for sub-30 nm organic defect monitoring.

Figure 17 shows AFM images of PSL nanoparticles dispersed on a Si substrate with a diameter size  $\sim$ 35 to 30 nm. By co-localizing the Raman laser beam with the AFM tip, we were able to confirm that the laser beam is probing PSL nanoparticles on the Si surface. Due to their small size and low abundance on the substrate, the nanoparticles were not detected by conventional micro- Raman even with full laser power (ca. 10 mW) and 1 sec integration time (Figure 18a). Instead, the Si signal saturates the detector. In contrast, upon dispersing the PSL nanoparticles on our gold template, characteristic Raman vibrational modes of PSL are clearly observed (Figure 18b) using the same acquisition condition.

 $HfO_2$  is a well-known gate dielectric material for pushing device performance beyond the 45 nm technology nodes. Monitoring the composition and crystal phase are of great interest to process and integration engineers, because both have an impact on the dielectric constant of  $HfO_2$  and therefore performance of the final device. Most of these parameters are currently monitored using X-ray based metrology, but the relatively large spot size in in-line X-ray (in micron size) precludes direct device monitoring. Raman has a smaller spot size and has higher sensitivity toward composition and crystal phase thus making it a potential metrology. Unfortunately,  $HfO_2$  has very weak Raman response. In this work we obtained Raman spectra from monoclinic  $HfO_2$  nanorods [10] using our gold pyramid. Figure 19a indicates that even with a 4 min acquisition time, no discernible Raman signal was obtained for the  $HfO_2$  nanorods on glass, whereas under the same excitation power distinct signals for monoclinic  $HfO_2$  were visible upon integration for just 1 min (Figure 19b). Figures 18b and 19b clearly indicate the plasmonic enhancement of Raman signals facilitated by our gold coated template and also indicate the potential of TERS for monitoring sub 30 nm carbonaceous defects and  $HfO_2$  directly on the device.



Figure 17 a) AFM map and b) Cross-Section of PSL Nanoparticles



Note: Both spectra were collected using full laser power ( $\lambda$ =633nm) and a 1 sec integration time.

Figure 18 Raman Data Acquired for PSL Nanoparticles Dispersed on a) Silicon Substrate and b) Gold Pyramids



Note: Both spectra were collected using full laser power (λ=633nm) a) signal integration time 4min
b) signal integration time 1min



Figure 19 Raman Spectra acquired for  $HfO_2$  nanorods dispersed on a) Glass and b) Gold Pyramids and c) Lattice-resolved HRTEM Image of an Individual  $HfO_2$  Nanorod. Reproduced from reference [10]

#### 5. Conclusion and Future Work

This work addresses several major challenges which limit the application of TERS for routine measurements: the lack of comparability, reproducibility, calibration, and standardization. For comparability and standardization, we demonstrated the potential to use an HVM FinFET processes to mass produce robust test structures. The SiGe test structure fabricated has sub-30 nm line width with height down to 5 nm (based on TEM) and we have shown that the design is stable and works well to test the spatial resolution and signal enhancement of a commercial TERS tool. Cross laboratory evaluations show that the test structures are very repeatable and have potential application for tool matching. To address reproducibility, we optimized a process proposed by Johnson et al., [9] which has the potential for mass production of a template for coating TERS tip by adding electrochemical etch, resulting in a 90% yield. We are still optimizing the final step, which will use PDMS as an adhesive to bind the gold pyramid shaped coating to AFM cantilevers. Success at

Proc. of SPIE Vol. 9424 94241S-12

this step will be a breakthrough for the TERS field and a leap forward for routine measurement. The second part of this work shows our gold template generates sufficient Raman signal enhancement for identification of sub-30 nm organic nano-particles and sub-10 nm hafnium dioxide nano-rod. The former result shows the potential of TERS for defect metrology by providing identification of carbonaceous species. The latter result shows the potential of TERS for on device monitoring of HfO<sub>2</sub>.

#### 6. References

[1] Sun, W. X., and Shen, Z. X., "A Practical Nanoscopic Raman Imaging Technique Realized By Near-field Enhancement," Mater. Phys. Mech. 4, 17-21 (2001).

[2] Saito, Y., Motohashi, M., Hayazawa, N., Iyoki, M., and Kawata, S., "Nanoscale characterization of strained silicon by tip-enhanced Raman spectroscope in reflection mode," Appl. Phys. Lett. 88, 143109 (2006).

[3] Zhu, L., Georgi, C., Hecker, M., Rinderknecht, J., Mai, A., Ritz, Y., and Zschech, E., "Nano-Raman spectroscopy with metallized atom force microscopy tips on strained silicon structures," J. Appl. Phys. 101. 104305 (2007).

[4] Hermann, P., Hecker, M., Chumakov, D., Weisheit, M., Rinderknecht, J., Shelaev, A., Dorozhkin, P., Eng, L. M., "Imaging and strain analysis of nano-scale SiGe structures by tip-enhanced Raman spectroscopy," Ultramicroscopy, 111, 1630-5(2011).

[5] Okuno, Y., Saito, Y., Kawata, S., and Verma, P., "Tip enhanced Raman Investigation of Extremely localized semiconductor-to-metal Transition of a Carbon Nanotube," Phys. Rev. Lett. 111, 216101(2013).

[6] Kohlgraf-Owens, D.C., Sukhov, S., and Dogariu, A., "Mapping the mechanical action of light," Phys. Rev. Lett. A84, 011807 (2011).

[7] Ramos, R., and Gordon, M. J., "Near-field Artifact In Tip Enhanced Raman Spectroscopy," Appl. Phys. Lett. 100, 213111 (2012).

[8] Schultz, Z., Stranick, S. J., and Levin, I.W., "Advantages and Artifacts of Higher Order Modes in Nanoparticle-Enhanced Backscattering Raman Imaging," Anal. Chem. 81, 9657 (2009).

[9] Johnson, T.W., Lapin, Z.J., Beams, R., Lindquist, N.C., Rodrigo, S.G., Novotny, L., and Oh, S. H., "Highly Reproducible Near-Field Optical Imaging with sub-20 nm Resolution Based on Template-Stripped Gold Pyramids," ACS Nano. 6 (10), 9168–9174. 2012

[10] Depner, S. W., Cultrara, N. D., Qin, Y., Farley, K. E., and Banerjee, S., "Organization of Ferroelastic Domains and Precursor Control of Size in 1D HfO2 Nanorods, ACS Nano. 8, 4678–4688(2014)