

Tip-enhanced Raman spectroscopy of single semiconducting nanostructures

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Tip-enhanced Raman spectroscopic (TERS) technique is reviewed for studying single semiconductor nanostructures along with different possible modes of operation in various optical arrangements. The role of scattering efficiency in the nanospectroscopic localized study using TERS in the near-field was explored for different inorganic covalent and partially ionic bonded Si, GaN and AlN single nanowires. A localized study was also performed for phase identification and dopant analysis in a single GaN nanowire. In the polarized TERS measurement, metal-insulator phase transition, along with the observation of spin-wave in a single VO₂ nanorod, was also explored. The size-dependent phonon population of single Si nanowires is also examined using TERS in the context of carrier depletion in these nanostructures. © Anita Publications. All rights reserved. doi:10.54955/AJP.33.1-2.2024.17-26.

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1 Introduction

Raman scattering is a very weak scattering process with intensity $\sim 10^{-5}$ of the illuminating laser intensity. Thus, the inelastically scattered intensity from a few molecules is negligible. However, the Raman intensity can be enhanced by increasing the electric field interacting with the few molecules using surface plasmons of noble metal nanoparticles as they are excited with laser light having energy matching the plasmon resonance frequency [1]. The Raman enhancement factor is proportional to the fourth power of the electric field. Therefore, the resonant light coupled with localized plasmons of metallic nanoparticles can generate a 'hot spot' leading to the enhancement of scattering intensity. In general, the plasmon enhanced inelastic scattering of light known as surface enhanced Raman scattering (SERS) is utilized for the spectroscopic study of nanostructures [2]. Tip enhanced Raman scattering (TERS) is a spectroscopic imaging technique which utilizes both scanning probe microscopy (SPM) and plasmonic-assisted SERS with the help of a metallic nanoparticle molded on the tip [3]. SPM aids in achieving spatial resolution and surface topology down to pico-meter using a feedback mechanism of interacting force or a tunneling current between a sharp tip and the sample surface. The tip and sample surface are scanned relative to each other while controlling the desired gap between them. Depending on the SPM mode, one can extract

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information on various electronic properties of the samples, namely, distribution of the density of states, surface potential, contact resistance while operating the tunneling current feedback (scanning tunneling microscopy, STM) and mechanical, local frictional, and acoustic properties in plasmon the force feedback configuration (atomic force microscopy, AFM) [3]. In its second component of SERS, plasmonic-assisted light also manifests into a nano-focused beam in the near-field, achieving the sub-diffraction limit [2]. In the TERS configuration, the SPM tip is either coated with noble metal (Au, Ag) or attached with a noble metal nanoparticle in different configurations. Thus, in TERS measurements, specially designed SPM tip guided incident light can be focused on a nanometric scale and can be utilized for Raman spectroscopic analyses for crystallographic phase, strain and electronic properties of structures down to single nanostructure.

In 1928, Sygne first reported the use of a single noble metal nanoparticle or a noble metal surface with a nanoscale aperture for sub-diffractive optical microscopy [4]. However, the first report of an experimental TERS study was published almost 75 years ago by Stokle *et al* [5]. Following the first experimental report, TERS imaging was demonstrated for local strain measurements in single walled carbon nanotubes (SWNTs) [6] and defect studies in the graphene layer [7]. Single molecule level sensing using TERS was demonstrated by M. D. Sonntag *et al* [8] in Dwyne's group. Following the report, a submolecular resolution was reported in an organic heterocyclic compound by Zhang *et al* [9] in Dong's group using scanning tunneling microscopic tip assisted-TERS study conducted in ultra-high vacuum taking the field to a new height.

2 Basic principle, enhancement mechanism and experimental design of TERS

Thus, the TERS study exploits both spatial resolution guided by the SPM tip and the sub-diffraction optical resolution achieved using plasmonic properties of the noble metal adhered to the SPM tip. Spatial resolution alone would not be useful for the diffraction limited light to achieve atomic resolution in Raman spectroscopic imaging.

TERS can be operated in two different configurations, namely, scattering and gap modes. In the scattering mode, light is incident on the noble metal coated/nanoparticle attached tip, and in the proximity of the sample surface, an evanescent wave is formed for achieving 'super-lensing' at near-field to focus the light to nanoscale [4]. The scattered inelastic light is collected at the far-field for Raman spectroscopic analysis. Scattering mode TERS was reported by directly coating brilliant cresyl blue and C60 fullerenes onto the glass substrate, where the enhancement was achieved by the tip alone [5]. On the other hand, a sample is placed on a noble metal substrate while a noble metal coated/nanoparticle attached tip is used to make a 'hotspot' in the gap of noble metal surfaces. The gap mode TERS demonstrates significantly higher enhancement of the Raman signal as compared to the scattering mode. Thus, nanostructures that can fit into the few-to sub-nanometer gap between the tip and the substrate, namely, 0-D nanocluster, 1-D nanowire (NW) and 2-D monolayer, show the strongest enhancement. A gap mode TERS of Rhodamine 6G molecules absorbed on Ag film using an Ag-coated Si tip has been reported [10].

TERS study can be conducted in various optical arrangements depending on the directions of light incidence to the sample-tip proximity and collection of the elastically scattered light for Raman analysis. In one of the well-practised arrangements, transmission mode illumination and collection is reported where a laser beam is focused on the sample in close proximity to the noble metal coated SPM tip through the objective located below the transparent sample and scattered Raman signal is collected with the same objective. The advantage of this configuration was achieving the highest numerical aperture of 1.4 for the oil-immersed objectives. In another prominent technique, a top illumination and collection are used for the TERS study. A bent noble metal coated tip is used for accessing the sample in close proximity to the tip. The same objective is used in this conformation. Limited access to the sample, actually in the proximity of the plasmonic tip, is a major disadvantage of the mode. However, the recent development of a bent tip

with noble metal nanoclusters at the tip is used for TERS study in the backscattering arrangement. Using a bent tip, top illumination of the incident light, and side collection of the elastically scattered light is another prominent scheme. Different objectives for focusing the incident light and collecting the scattered light are used in this arrangement.

The enhancement factor (EF) of TERS is estimated using the relation expressed in the Eq (1) of [11]

$$EF = \left(\frac{I_{with-tip}}{I_{without-tip}} - 1 \right) \frac{V_{FF}}{V_{NF}} \quad (1)$$

where $I_{with-tip}$ and $I_{without-tip}$ are the recorded Raman mode intensity in the presence and absence of the TERS probe in the near-field, respectively. V_{NF} is the effective interaction volume created by the near-field evanescent waves in the presence of the TERS probe, and V_{FF} is the sample-laser excitation interaction volume in the far-field. Generally, a cylindrical interaction volume in the near-field configuration is $V = \delta \cdot \pi r^2$, where δ is the penetration depth of laser excitation through the sample and r is the radius of the cylindrical interaction volume. In the case of the near-field Raman spectral acquisition, the presence of the TERS probe may confine the laser light and concentrate the field strength into a spot with a diameter of ~ 10 - 100 nm. Therefore, V_{NF} is found to be $\sim 10^4$ - 10^6 nm³ by assuming that the evanescent waves can penetrate the sample up to a distance of the order of a half-wavelength of visible light. However, for the far-field configuration, cylindrical interaction volume cannot be considered, as the focused laser beam diameter (~ 1 μ m) is generally one to two orders larger than the diameter of the nanorod (~ 10 - 100 nm). So, one can consider the interaction volume of the nanorod by the exposed laser beam as a rectangular prismoid.

3 Factors influencing the signal enhancement and imaging of single nanostructures

Along with plasmonics, dielectric microcavities are also used for the nanoscale focusing or imaging in the sub-diffraction limit utilizing by the strong confinement or amplification of the light [12]. Though optical micro-cavities confine the electromagnetic radiation in a process of multiple reflections and standing wave formation, they are diffraction limited. In this regard, resonators and noble metal nanostructures have shown better prospects than dielectric microcavities to overcome the diffraction limit [13]. The localized electromagnetic waves, spreading along metal-dielectric interfaces as surface plasmon polariton (SPP), can be confined and used for imaging in the sub-diffraction limit [14].

In the case of nanospectroscopy, TERS is a useful technique to study different organic and bio-molecules, carbonaceous nanostructures, and crystallites [15]. The reported TERS EF is as high as nine orders for organic single molecules [8]. Apart from illumination and collection geometry of the TERS setup and tip geometry, as discussed earlier, enhancement of Raman scattering intensity and spatial resolutions in spectral imaging are limited by several other factors, such as tip-sample proximity coupling of incident light and polarization states of the electromagnetic fields of excitation source as well as the metallic tip [16]. A wide range of EFs from three to nine orders high and spatial resolutions ranging from tens of nm to sub-nm are reported for different analytes.

Even though the experimental constraints prevail, the Raman scattering efficiency, inherent to analyte properties, is another limiting factor to achieving high EF and contrast variation in spectroscopic imaging techniques. In this regard, the nature of the chemical bonding of the analyte and its polarizability with respect to the excitation source influence the Raman intensities. Many researchers demonstrated various capabilities of TERS using mainly covalently bonded organic molecules of porphyrin, brilliant cresyl blue, Rhodamine 6G, Thiophenol or carbonaceous nanostructures of CNTs and graphene as these molecules demonstrate very high Raman scattering efficiency of nearly thirteen order enabling them for single molecule Raman imaging [5-9]. However, TERS studies of covalent bonded inorganic crystallite such as Si with fractional ionic character (FIC) value of nearly zero showed EF of three to four orders high with a few reports on

single nanostructure imaging [17,18]. Similarly, the III-nitride crystallites of particularly GaN and AlN with FIC values of 0.5, and 0.7 (FIC = 1 for pure ionic crystal), respectively, showed negligibly low enhancement of Raman intensities [19,20]. Until our studies in 1-D GaN and AlN nanostructures, there was only one report on single nanostructure TERS analysis of GaN imaging of $\text{In}_x\text{Ga}_{1-x}\text{N}$ [20]. In fact, not a single study on Raman enhancement of AlN is reported, as AlN is an inorganic crystalline solid possessing the highest ionicity (FIC ≈ 0.72) among other group III nitrides.

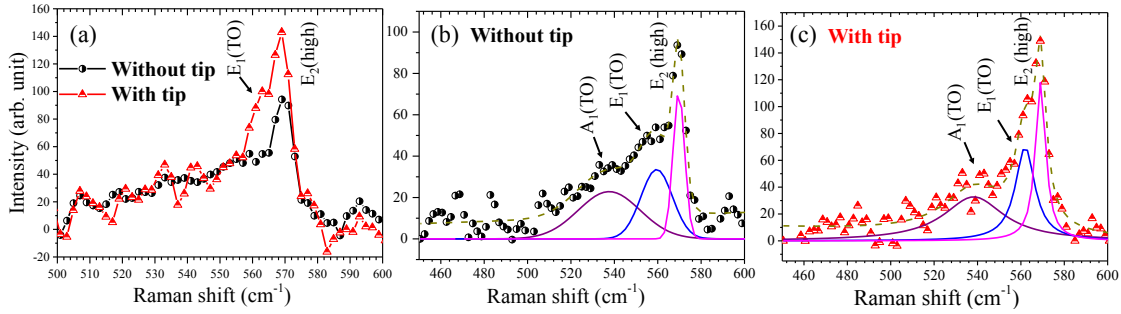


Fig 1. (a) Raman spectra of a single GaN NW with and without the tip. Deconvoluted Raman spectra collected at a single scan area on the GaN NW (b) without and (c) with the assistance of TERS tip. (Reproduced from Ref [21] with the permission of AIP Publishing).

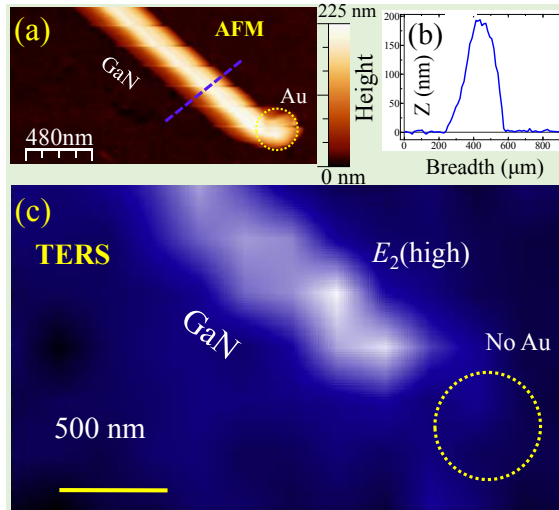


Fig 2. (a) AFM image of a single GaN NW with the corresponding (b) line profile showing the height of the NW as ~ 200 nm (c) The corresponding TERS image of the single NW mapped with the intensity distribution of the E_2 (high) mode. Catalyst Au nanoparticle at the tip (a) is not visible in the spectroscopic image. (Reproduced from Ref [21] with the permission of AIP Publishing).

In one of our TERS studies, we reported properties of a single ~ 200 nm diameter GaN NW far below the diffraction limit of 750 nm using Ar^+ laser of 514.5 nm excitation and microscope objective with a numerical aperture 0.42 nm [21]. An apertureless TERS probe was used for the TERS study with an Au nanoparticle (~ 100 nm) attached on the probe tip. These GaN NWs were grown by the chemical vapor deposition (CVD) technique using Au as a catalyst following vapour-liquid-solid (VLS) process. Au metal nanoparticles are often seen in the tip of the NWs. In top illumination/collection configuration of Au nanoparticle assisted TERS mode, the nanoscopic imaging of a single GaN NW laid on a polished single Al crystal substrate was performed.

One-order higher EF values (~ 13 - 31) were recorded for the observed Raman modes, as expected for an ionic compound with FIC value of 0.5. A small variation of EFs for various observed Raman modes is ascribed to the molecular arrangement with respect to the TERS enhanced electric field. Similar properties of single GaN NWs were earlier studied without any report of spectroscopic imaging [19,22]. In our study [21], we also report nanospectroscopic imaging of ~ 200 nm diameter single GaN NW (Fig 2).

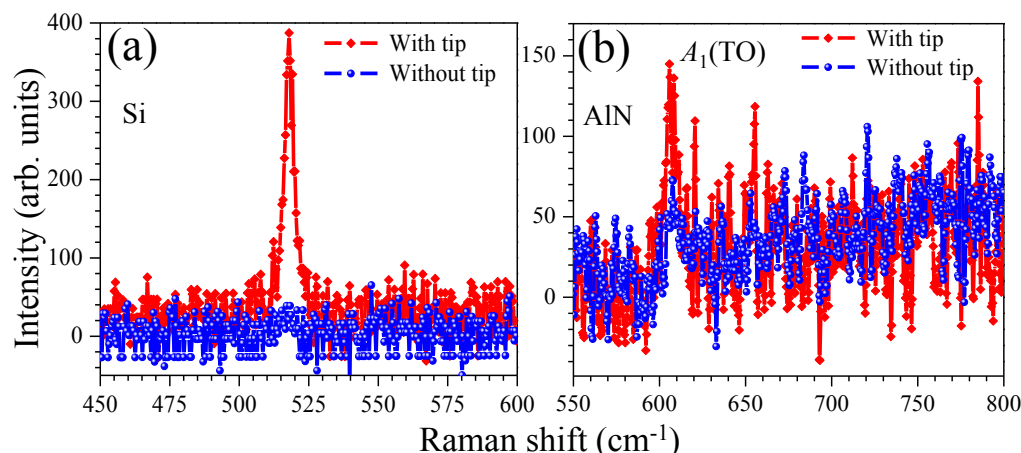


Fig 3. Single-spot Raman spectra of semiconductor nanostructures for far-field (without tip) and near-field (with tip) configurations (a) Si NW with an acquisition time of 1s, (b) AlN NT with an acquisition time of 5s. (Reproduced from Ref [23] with the permission of ACS Publications).

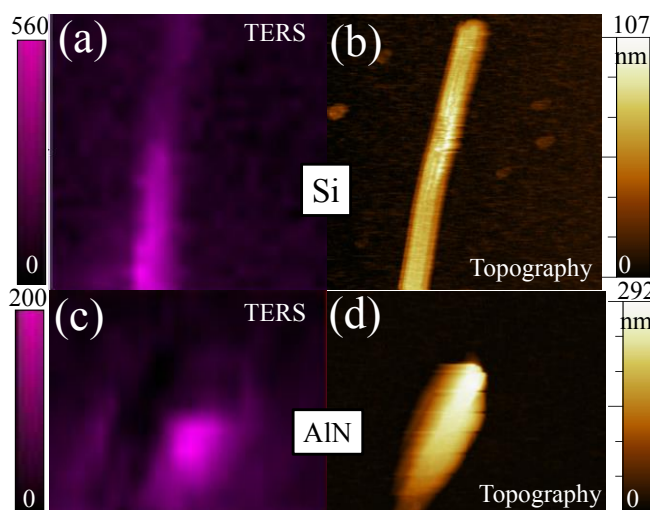


Fig 4. Near-field (a) TERS and corresponding (b) topography map of Si NW; (c) TERS and corresponding (d) topography maps of AlN nanotip. The color scale bars indicate the variation in the intensity of the Raman-allowed mode (left) and height (right) along the nanostructures. (Reproduced from Ref [23] with the permission of ACS Publications).

Nanospectroscopic Raman imaging of single GaN NW, for the first time, was possible as we could effectively confine the 514.5 nm excitation by choosing Al as a back reflector to minimize the scattering intensity loss in order to maximize the Raman intensity. Based on the knowledge of wavelength-dependent reflectance and optical constants of well-known plasmonic metals, a polished Al single crystal was chosen as it shows one of the highest reflectance of incident and scattered photons of 514 nm.

We also studied two important inorganic nanostructures, Si NW and AlN nanotip, using TERS. The TERS spectra of both Si NW and AlN nanotip show an enhancement in the presence of a plasmonic TERS probe [23]. However, plasmonic enhancement of Raman mode for the 50-60 nm diameter Si NW (Fig 3a) collected even for an acquisition time of 1s is significantly higher than that for AlN nanotip (Fig 3b) of varying diameter in the range of 70-250 nm collected over 5 s. The EFs of Si-NW and AlN nanotip were calculated as four and one order higher, respectively.

Because of the high TERS EF value corresponding to the Raman mode of Si, strong contrast and matching of the exact topography (Fig 4a) were observed along the NW in the nanospectroscopic TERS image (Fig 4b). On the other hand, in the case of AlN nanotip even with higher dimension (Fig 4c,d), the resolution of the TERS image was poor. The results clearly indicated that the Raman scattering efficiency was higher for the covalent bonded nanostructures compared to that of ionic bonded ones, even in the presence of plasmonic enhancement effects. In effect, the report is a successful demonstration of the role of Raman scattering efficiency of the analyte for spectroscopic imaging of inorganic nanostructures using TERS technique.

4 TERS as a local probe to study single nanostructures

4.1.1. TERS study of defect induced phonon modes in semiconducting nanowires

Along with undoped NW, the TERS study of the O and Mg-doped single GaN NW was also reported in the sub-diffraction limit [22]. GaN nanowires with the O impurity and the Mg dopants were grown by the CVD technique in the VLS process using Au as a catalyst.

The TERS spectrum of O-rich GaN showed symmetry allowed modes of $A_1(\text{TO})$, $E_2(\text{high})$, and $A_1(\text{LO})$ phonon modes, along with weak zone boundary (ZB) modes and mode related to impurity phase of oxy-nitride (Fig 5a). The absence of stoichiometric oxide phase in the TERS study indicates O incorporation was in the form of native defect occupying N (ON) site or in the formation of complexes with N vacancy (VN), which contributed to the carrier generation of the electron in GaN NWs. A strong coupling between LO phonons and electron carriers generated by ON and VN in the NWs was evidenced by the observed asymmetric broadening of the $A_1(\text{LO})$ mode [22].

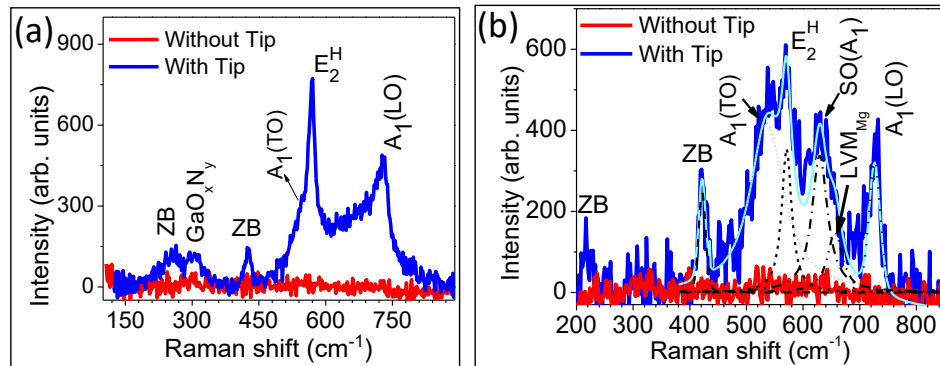


Fig 5. TERS spectra of (a) O-rich single GaN NW, (b) Mg-doped single GaN NW without and with TERS tip (Reproduced from Ref [22] with the permission of AIP Publishing).

Strong intensities were observed for the symmetry allowed modes in the TERS spectrum of a typical single Mg doped single GaN NW (Fig 5b). Additional peak corresponding to surface optical mode at 633 cm^{-1} owing to surface defects was observed for both the undoped and Mg doped GaN NW. A weak local vibrational mode at 656 cm^{-1} corresponding to Mg doping in GaN confirmed the presence of Mg as a

dopant in the single GaN nanowires. Strong intensities of the non-zone center ZB modes (Fig 5b) were also observed for the TERS studies of both the pristine and doped GaN NWs in the absence of strong electron-phonon coupling in the presence of native defects as observed for GaN NWs with significant O impurity (Fig 5a) [22]. Thus, the TERS can be used for the localized effects by impurities in a single nanowire for developing the nanowire based electronic and optoelectronic devices.

4.1.2 TERS study of structural phase transition in single nanorods

Polarized Raman spectroscopy combined with TERS is capable of confirming the crystalline phase as well as the crystallographic orientation sample of nano-dimension. Moreover, the identification of Raman mode frequency accountable for the structural phase transition is also possible as the technique is efficient with directional field enhancement.

Phase transition in a single VO₂ nanorod was reported using polarized TERS studies in the backscattering configuration (Fig 6). A typical 1D VO₂ nanorods lying horizontally were studied for the polarized TERS measurements [24]. The growth direction along the long axis of the nanorods was chosen as the X direction, and the TERS study in the backscattering mode was performed in the Z direction. The parallel, Z(XX)Z, and perpendicular, Z(XY)Z, polarizations configurations were met using a half-wave plate and a polarizer. The far-field and the near-field measurements were carried out at 300 K. At two different conditions of parallel (XX) and cross (XY) polarizations, the near- and far-field Raman spectra of single-crystal VO₂ were plotted (Fig 6a,b). Among the observed twelve mode frequencies, Raman modes observed at 189 and 220 cm⁻¹ were reported to evolve because of the V–V vibration. The intensity ratio of the two Raman modes close to 200 cm⁻¹ flips between parallel and cross-polarization conditions, indicating that the phonon modes are normal and parallel to the orientation of V–V dimer.

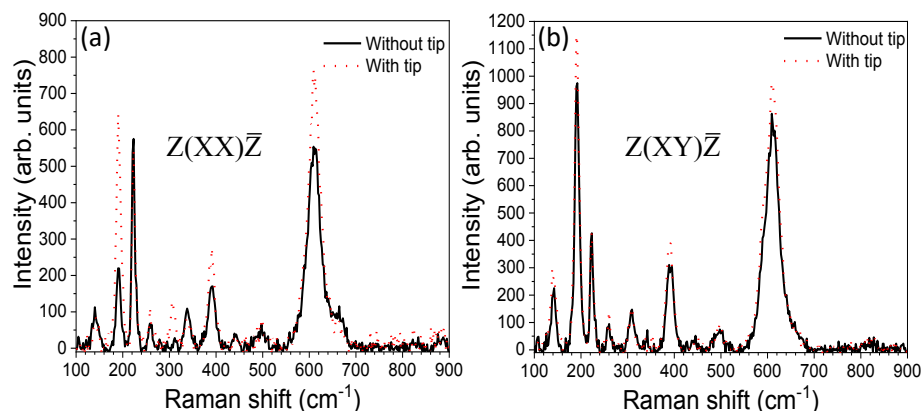


Fig 6. Raman spectra at (a) parallel Z(XX)Z polarization with (dotted line) and without (solid line) TERS tip and (b) Raman spectra at cross Z(XY)Z polarization with and without TERS tip. (Reproduced from Ref [24] with the permission of ACS Publications).

The 1D VO₂ nanorods are oriented by the (011) face, and their growth direction is along the [100] for the monoclinic M1 phase. Thus, the V–V interaction along the [100] direction (X-axis) and in the normal direction (Z-axis) led to the Raman mode frequencies at 189 and 220 cm⁻¹, respectively.

The Raman mode at 189 cm⁻¹ in the polarized TERS studies (Fig 6a) showed significant enhancement in parallel conditions and less in cross-polarization conditions. However, there is hardly any enhancement for the Raman mode at 220 cm⁻¹ in both the polarization conditions confirming growth orientation of the 1D VO₂ nanorod as well as demonstrating the unique property of directional enhancement in TERS. Thus, the assignment of individual Raman modes, particularly those responsible for the phase transition

in VO₂, was accomplished using the polarized TERS studies. In a detailed study, temperature dependent TERS studies confirmed that the departure of V–V dimers along the [100] direction was responsible for the structural phase transition from the M1 to the monoclinic M2 phase of VO₂ at 330 K, without inducing metallicity in the system. The origin of low-frequency Raman modes as spin-wave in VO₂, for the first time, was confirmed from the orthogonal dependency of the phonon and spinon vibration in the polarized Raman measurements [25,26]. The observation of low-frequency spin-wave mode in both insulating M2 and metallic states confirmed the ineffectiveness of spin-Peierls dimerization, bringing metallicity in VO₂. On the contrary, the Mott–Hubbard picture dominates the metal-insulator transition (MIT) in VO₂, where the Peierls (spin-phonon) instability arises subsequent to the MIT.

4.1.3 TERS study of phonon population in single semiconducting nanowires

We report the TERS study of optical phonons in Si NWs with sizes beyond the phonon confinement regime [18]. A peak shift and asymmetric broadening by phonon mode in Si NWs was recorded in the far-field Raman studies. In the TERS measurements, size-dependent single to multiple phonon peaks in Si NWs were also recorded (Fig 7).

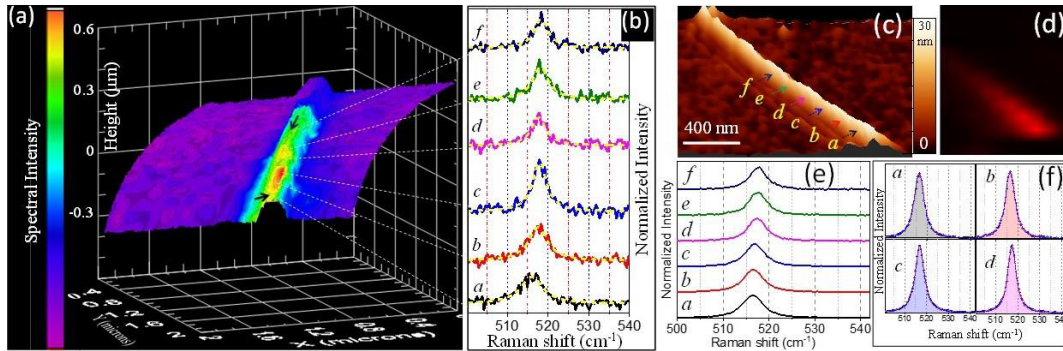


Fig 7. (a) TERS map overlaid on its corresponding 3D height map of Si NW having a diameter ~ 60 nm. Color scale indicates the relative spectral intensity of TERS map. (b) TERS spectra picked from the recorded map at different locations along the NW showing broadened asymmetric peaks. The dashed lines represent the Lorentzian fits of respective curves. (c) 3D topography map of the single Si NW having a diameter ~ 25 nm. (d) 2D TERS intensity imaging of the ~ 25 nm NW. Very low Raman intensity at the end of the NW showing possible drift in the position of TERS tip from laser spot during the period of scanning. (e) TERS spectra recorded with an acquisition time of 10 s at different locations (a–f) along the NW, and (f) the corresponding Lorentzian profile fitted curves at locations a–d showing single peak. (A portion of the data reproduced from Ref [18] with the permission of ACS Publications).

Conducting a TERS study of single Si NW with proper thermal management using a conducting substrate of Au/Cr coated silica cover slide, we established the decoupling of multiple origins, namely, shape and size effect, thermal and Fano broadening of phonon mode responsible for the appearance of multiple phonon peaks accompanied by peak shift and asymmetric broadening of the Raman mode. We could explain the redshift accompanied by asymmetric broadening and the multiple phonon modes in larger diameter Si NWs of ~ 60 nm (Fig 7b) by using a model based on the localized phonon populations prompted by the charge depletion in the NW depending on its diameter [18]. Full-width half maxima (FWHM) of ~ 5 and 9 , having phonon lifetimes of ~ 1 and 0.6 ps, respectively, were rerecorded for the ~ 60 nm Si NW. The size-dependent charge depletion in NWs is further confirmed by surface potential measurements on single NWs of various diameters. The smaller diameter Si NW (~ 25 nm) was found with carriers completely depleted, showing a very low value of surface potential. Simultaneously, a single one-phonon mode with FWHM ~ 5 (phonon lifetime ~ 1 ps) throughout the NW (Fig 7c) was recorded for the ~ 25 nm Si NW.

5 Summary and outlook

We reviewed tip enhanced Raman spectroscopy (TERS) as a technique to probe semiconductor nanostructure properties at the nanoscale using plasmonics surface probe microscopic tip where light can be focused in the sub-diffraction limit forming evanescent wave in the near-field. Various types of TERS configurations, namely, scattering and gap modes used in different optical arrangements of back, top or side illumination/collection, were discussed in the introduction. A generally accepted formalism for calculating the enhancement factor is also deliberated. We also elaborated on the role of scattering efficiency of different analyte chemical bonds in the nanospectroscopic TERS studies. Difficulties of studying analytes with inorganic covalent as well partially ionic bonds are deliberated with few case studies for Si, GaN and AlN nanostructures. AlN, being close to the characteristics of pure ionic bonds, showed the poorest nanospectroscopic images in the TERS measurement. The study offers an understanding of the role of scattering efficiency in the resolution of near-field spectroscopic imaging. Finally, a few localized studies are reviewed, of which defect studies in GaN nanowires helped identify the presence of O as an impurity and Mg as a dopant. Thus, doping in semiconductors, even at low levels, can be probed in the near-field measurements and help in device fabrication. Polarized TERS measurement helped to identify metal-insulator phase transition in VO₂ nanorods along with the identification of a unique low-frequency spin-wave mode. Thus, phase transition can be very well studied in the localized measurement of polarized TERS. In an exclusive near-field TERS study, we explored the phonon population in a single Si nanowire prompted by the charge depletion in the NW depending on its diameter. One-phonon with single and minimum broadening was observed for Si nanowires with diameters below 25 nm, where charge carriers were found to be completely depleted. The study clearly suggests that the size-dependent phonon characteristics of semiconductor nanostructures are important to study in the near-field for various applications involving their electrical characteristics, namely, thermoelectric and photovoltaic devices.

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