Tip-Enhanced Raman Scattering of Nanomaterials*

Sanpon Vantasin

*Department of Chemistry, School of Science and Technology,
Kwansei Gakuin University, Sanda, Hyogo 669-1337, Japan*

Xin-lei Yan

National Institute of Advanced Industrial Science and Technology (AIST), Nagoya, Aichi, Japan

Toshiaki Suzuki

UNISOKU Co., Ltd., 2-4-3, Kasugano, Hirakata, Osaka 573-0131, Japan

Yukihiro Ozaki†

*Department of Chemistry, School of Science and Technology,
Kwansei Gakuin University, Sanda, Hyogo 669-1337, Japan*

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Various kinds of carbon nanotube-based and graphene-based nanomaterials are considered as future materials for electronic devices due to their outstanding properties. This review paper reports tip-enhanced Raman scattering (TERS) studies of polymer nanocomposites containing carbon nanomaterials and graphenes. TERS is an emerging spectroscopic tool that combines scanning probe microscopy and Raman spectroscopy. Compared with normal Raman spectroscopy, TERS has much better spatial resolution and sensitivity. The usefulness of TERS technique in studying structure and interactions of nanomaterials is demonstrated by introducing four TERS studies. [DOI: 10.1380/ejsnt.2015.329]

Keywords: Tip-enhanced Raman scattering; Raman spectroscopy; Graphene; Polymer nanocomposites; Nanomaterials

I. INTRODUCTION

Nanomaterials such as graphenes [1–4] and carbon nanotubes [5–7] have been the focus of a wide variety of researches because of their unique material properties, for example, charge carrier mobility, optical transparency, and elasticity. The nature of nanomaterials is altered by interactions with substrates and the distortion of the local structure. Therefore, it is of particular importance to explore the interaction and distortion in very small areas of the nanomaterials.

Raman spectroscopy has widely been used for the above purpose [8–11]. Raman spectra of graphenes and carbon nanotubes change with their structure, defects, and strain. The numbers of layers, structure, and defects of graphenes have been investigated by using peak shifts, intensity variations, and changes in band width [10–15]. Moreover, Raman imaging measurement allows visualizing local structure distribution of graphenes and carbon nanotubes [16–18]. A Raman spectrum of graphene is mainly characterized using three representative signals called G, G', and D bands, which are observed at about 1600, 2700 and 1350 cm^{-1} , respectively [8–11]. G band is originated from doubly degenerate (E_{2g}) LO and iTO phonons around Γ point, while G' band is a result of double resonance process consisting of two scatterings of iTO phonons around K point. The D band is due to defects in graphene, allowing us to investigate the structure of defects. The spatial resolution of Raman scattering is restricted by the diffraction limit of light. Usually it is 500

nm to $1\mu\text{m}$. On the other hand, the spatial resolution of tip-enhanced Raman scattering (TERS) is determined by the radius of a tip and can exceed the diffraction limit of light [19, 20]. TERS is a technique that employs near-field enhancement from a metallic nanotip to obtain Raman spectra with spatial resolution surpassing the diffraction limit [21–26]. The enhancement field from plasmon resonance is confined to a small area around the tip, resulting in the improvement of spatial resolution. A typical interesting feature of TERS is that it allows molecular-scale view of small ensembles of molecules or even single molecules. Thus, it has been proved that TERS is a unique technique for probing very small portions of complicated materials such as graphenes and carbon nanotubes [27–46].

Saito *et al.* [35] measured TERS spectra of the edge boundary of exfoliated graphene fabricated on Si with a spatial resolution of 30 nm. They investigated position-dependent TERS spectra and found G band shifts arising from an excess charge effect and D band peak fluctuations due to the local strain distribution within the layers. Wang *et al.* [37] performed a TERS study of exfoliated graphene by using a TERS probe consisting of gold nanoparticles. They induced reversible artificial defects and controlled them using the TERS probe. However, TERS investigations of the exfoliated graphene have a difficulty in controlling the graphene properties due to mechanical distortion. A few groups reported TERS studies of graphenes prepared by a silicon carbide (SiC) thermal decomposition method [47] and a chemical vapor deposition (CVD) method [48]. These methods can be used to prepare homogeneous graphene with higher quality in a larger area [49]. Suzuki *et al.* [40] reported a TERS study on stress change in the local domain of epitaxial graphene on the carbon face of 4H-SiC (000 $\bar{1}$) and Vantasin *et al.* [41] characterized sub-micro/nanostructures of

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† Corresponding author: ozaki@kwansei.ac.jp

epitaxial graphene on 4H-SiC (000 $\bar{1}$) using TERS. These studies will be introduced in some detail.

Among polymer nanocomposites, polymer/carbon nanotube (CNT) materials have attracted great interest because an addition of even small amount of CNTs into a polymer can improve the mechanical, physical, and electrical properties of polymers significantly [50, 51]. However, the mechanism by which the properties are improved has not been fully elucidated and the control of dispersion of CNTs in a polymer system is still a great challenge because of the high van der Waals interaction between neighboring CNTs and the large surface area of nanotube. The physical and chemical properties of polymer nanocomposites are greatly affected by the distribution and decentralization of the CNTs. These effects can be induced by the interaction between the polymer and nanofiller and/or a change in the local structure of the polymer [52, 53]. The interactions in nanocomposites occur at the interface between the polymer and nanofiller, and thus high spatial resolution, on the order of less than several tens of nanometers, is required to investigate the interactions. Raman spectroscopy is a powerful tool for the characterization of CNT-based materials but normal Raman experiments can determine only average information from nanocomposites. Thus TERS is expected to play an important role in exploring the interfacial structure and interaction of polymer composites including CNT-based nanocomposites. The local molecular interactions on the interface of styrene-butadiene rubber (SBR)-multiwalled carbon nanotube (MWCNT) nanocomposites were investigated by Suzuki *et al.* [54] by using TERS. Yan *et al.* [55] carried out a TERS study on the interaction of single-walled carbon nanotubes (SWCNTs) and polystyrene (PS) at the interface in the SWCNT-PS nanocomposites. These investigations will be outlined later.

The purpose of the present study is to demonstrate the potential of TERS spectroscopy in exploring structure and interactions of nanomaterials. As examples, two TERS investigations on polymer nanocomposites and those on graphenes are introduced to show the usefulness of TERS in characterizing individual local nanostructure on polymer nanocomposites and graphenes.

II. TERS STUDIES ON POLYMER NANOCOMPOSITES AND GRAPHENES

A. Tip-Enhanced Raman Spectroscopy Study of Local Interactions at the Interface of Styrene-Butadiene Rubber/Multiwalled Carbon Nanotube Nanocomposites

TERS spectra were measured for SBR and MWCNTs nanocomposite films to investigate the local molecular interaction between the polymer and the nanofiller [54]. The spectra collected from separated points in the nanocomposites were attributed to SBR or MWCNTs, demonstrating great potential for studying local film inhomogeneity within several tens of nanometers. It was noted that TERS bands due to SBR phenyl groups were strong when MWCNT bands were strong, whereas vinyl-group TERS bands were strong when the MWCNT bands

FIG. 1. Raman spectra of (a) pure SBR, (b) pure MWCNTs, and (c) 1 phr SBR/MWCNT nanocomposites. (From ref. [54].)

TABLE I. Assignment of Raman Bands of 1 phr SBR/MWCNT Nanocomposites (From ref. [54])

Wavenumber (cm ⁻¹)	Assignment
1004	phenyl ring breathing SBR (phenyl)
1032	phenyl ring stretching SBR (phenyl)
1354	D band MWCNTs
1604	G band MWCNTs
1641	cis C=C stretching SBR (C=C)
1668	trans C=C stretching SBR (C=C)
2698	G' band MWCNTs
2847	aliphatic CH symmetric stretching SBR (main chain)
2906	aliphatic CH asymmetric stretching SBR (main chain)
2990	vinyl C-H stretching SBR (C=C)
3064	aromatic C-H stretching SBR (phenyl)

were weak. Based on these observations it was concluded that the local distribution of polymer chains is modified with changes in the orientation of the phenyl rings by π - π interactions between the polymer chains and the MWCNTs [54].

Figure 1(a)-(c) shows Raman spectra of pure SBR, pure MWCNTs, and 1 phr SBR/MWCNT nanocomposites, respectively. [54] From a comparison of the three spectra in Fig. 1, Suzuki *et al.* made band assignments. The assignments are summarized in Table I [54]. Compared with the pure MWCNT spectrum, the G band in the SBR/MWCNT spectrum shifted to a higher wavenumber, suggesting the shrinkage of the CNTs induced by the pressure from the matrix of the polymer [56, 57].

Raman spectra of SBR/MWCNT nanocomposites observed under tip-approaching and tip-retracted conditions are shown in Fig. 2 [54]. The TERS spectrum was calculated by subtracting the spectrum observed under tip retracted conditions from that collected under tip-approaching conditions as shown in Fig. 2.

Figure 3(a) exhibits normal Raman spectra of 1 phr SBR/MWCNT nanocomposites collected at eight points

FIG. 2. (A) SR-SAXS and (B) SR-WAXD profiles of the binary mixture of PDMS and squalane at various mixing ratios (weight of squalane / weight of binary mixture).

(Point 1-8) [54] (The unit of 'phr' stands for parts per hundred parts of rubber by weight). The Raman spectra in Fig. 3(a) demonstrate point-dependent spectral variations. For example, the Raman signals of Point 7 assigned to SBR were relatively strong, while the spectrum collected at Point 3 yielded relatively strong MWCNT signals. However, both CNT and SBR signals were always observed at each point, and the point-dependent spectral differences were rather small. Figure 3(b) displays TERS spectra measured at the same points at which the Raman spectra in Fig. 3(a) were collected [54]. Note that the TERS spectra measured at the eight points were markedly different from each other. For example, in the spectrum at Point 7, TERS peaks at 2990, 2904, 2847, 1668, and 1641 cm^{-1} due to SBR appeared, however, TERS signal at 1354 cm^{-1} assigned to MWCNTs (D band) was considerably weaker than the corresponding peak in the Raman spectrum. The G band (1604 cm^{-1}) and G' band (2698 cm^{-1}) were not observed in the spectrum measured at Point 7, while at Point 3 TERS signals were observed at 3064, 2990, 2904, 2847, 2698, 1604, and 1354 cm^{-1} . The TERS signals at 3064, 2990, 2904, and 2847 cm^{-1} were ascribed to SBR, whereas those at 2698, 1604, and 1354 cm^{-1} come from MWCNTs. These results demonstrated the potential of TERS spectroscopy in probing position-dependent structural variations.

Figure 4(a) and (b) depict the 1800–800 and 3200–2500 cm^{-1} regions of TERS spectra obtained at Points 7 and 3 in Fig. 3(b), respectively [54]. In the corresponding Raman spectra for Points 7 and 3 in Fig. 3(a), the Raman band at 1004 cm^{-1} is more intense than those at 1668 and 1641 cm^{-1} . In contrast, for the TERS spectra, the latter bands were stronger than the former band (Fig. 4(a)). Moreover, in the higher-wavenumber region, four SBR bands appear at 3064, 2990, 2906, and 2847 cm^{-1} in the normal Raman spectrum (Fig. 3(a)). However, in the TERS spectrum in Fig. 4, the 3064 cm^{-1} band was nearly missing, and the relative intensity of the signal at 2990 cm^{-1} became stronger than that of the corresponding signal in the Raman spectrum. The bands at 3064 and 1004 cm^{-1} that were observed to be relatively weak in the TERS spectrum arose from the aromatic C–H

FIG. 3. (a) Raman and (b) TERS spectra of 1 phr SBR/MWCNT nanocomposites measured at the eight points. (From ref. [54].)

groups and the phenyl rings of the polymer side chains, respectively.

In contrast to Fig. 4(a), the TERS signals due to MWCNTs at 2698, 1604, and 1354 cm^{-1} appeared strongly in Fig. 4(b), and a peak at 3064 cm^{-1} assigned to aromatic C–H was clearly observed. In the TERS spectra, the intensity of the 2990 cm^{-1} signal (vinyl) decreased as the intensity of the 1604 cm^{-1} signal (G band) increased. On the other hand, the signal intensity at 3064 cm^{-1} (phenyl) increased as the intensity of the G-band signal increased (Fig. 4(b)). In the Raman spectra, both signals at 2990 (vinyl) and 3064 (phenyl) cm^{-1} increased with an increase in the intensity of the 1604 cm^{-1} signal. Suzuki *et al.* [54] suggested from these results that the local distribution of polymer nanocomposites at the interface between the polymer and the filler was different from that of polymer areas without MWCNTs.

Based on the observed results regarding the spectral variations induced by SBR, Suzuki *et al.* [54] proposed a structure and interaction of the surface of the SBR/MWCNT nanocomposites illustrated in Fig. 5. In areas of polymer nanocomposites without MWCNTs, it is likely that the C=C groups and the phenyl rings are parallel to the polymer surface. In this orientation, the C=C signal would be much more enhanced than that of the phenyl ring. On the other hand, at the interface of the polymer and the filler (Fig. 5(b)), it seems that MWC-

FIG. 4. Enlarged TERS spectra of 1 phr SBR/MWCNTs from Figure 3: (a) spectrum 7, (b) spectrum 3. (From ref. [54].)

FIG. 5. Schematic diagram of the surface structure of SBR/MWCNT nanocomposites: (a) far from and (b) near the CNT area. At the interface between the polymer and the filler, the phenyl ring should be oriented perpendicular to the surface through a π - π interaction between the CNT and the phenyl ring. (From ref. [54].)

NTs had a significant interaction with the phenyl rings of the polymer through π - π interactions. These interactions may induce differences in the orientations of the polymer chain and its side residue. The orientation of the phenyl rings at the interface is likely to be perpendicular to the surface because of the π - π interaction between the CNTs and the phenyl rings shown in Fig. 5(b). It seems that the TERS spectra detected these changes very clearly.

B. A Study on the Interaction of Single-walled Carbon Nanotube (SWCNT) and Polystyrene (PS) at the Interface in SWCNT/PS Nanocomposites by Tip-enhanced Raman Spectroscopy

Raman spectra of (a) pristine SWCNT and (b) SWCNT/PS composites are compared in Fig. 6 [55]. The pristine SWCNTs show four main peaks in the region of 3000–1000 cm^{-1} (Fig. 6(a)). The G band appearing in the 1600–1550 cm^{-1} region splits into two sub-bands. The shape of two G bands in Fig. 6(a) and previous studies suggest that the SWCNTs belong to a semiconductor type of CNTs. The peak at 1566 cm^{-1} is due to the G^- band, which corresponds to a carbon vibration along the circumferential direction, and that at 1595 cm^{-1} is assigned

FIG. 6. Raman spectra of pristine SWCNTs (a) and 0.5 wt.% SWCNT/PS composites (b). (From ref. [55].)

to the G^+ band, which arises from a carbon vibration along the nanotube axis.[58] A weak D band is observed near 1343 cm^{-1} . In the case of CNT, this band reflects defects or disorder such as amorphous carbons, vacancies, heteroatoms, and so on [59]. G^- band is located at around 2700 cm^{-1} .

Compared with the spectrum of the SWCNTs (Fig. 6(a)), that of the SWCNT/PS nanocomposites (Fig. 6(b)) shows shifts of several Raman bands of SWCNTs. In particular, the G^- shifts from 1566 to 1572 cm^{-1} , and G^+ band shows a smaller shift from 1593 to 1595 cm^{-1} , respectively. The G' band has the largest shift from 2658 to 2689 cm^{-1} . Based on previous Raman studies, Yan *et al.* [55] concluded that the shifts of the G and the G' bands reflect mechanical compression of the SWCNTs by the polymer. [60, 61]

Figure 7(a) exhibits Raman spectra of the SWCNT/PS composites measured at nine randomly collected points (P1, P2, P3, P4, P5, P6, P7, P8, and P9) in the G band region [55]. The Raman spectra do not show a point-to-point difference in terms of band positions and relative band intensities; the G band shows only a negligible shift of $< 2 \text{ cm}^{-1}$ at the different points. It is rather difficult to investigate the distribution of SWCNTs and the interactions at the interfaces between the SWCNTs and the PS from normal Raman spectra.

Figure 7(b) displays TERS spectra of the SWCNT/PS composites observed at the same points as those in Fig. 7(a). The TERS spectra at the nine points obviously change with the points. Figure 8(a) and (b) compare the peak positions of the (a) G^- and (b) G^+ bands between the far-field Raman spectrum and the TERS spectrum for each point [55]. The largest shift of the G^- peak is about 13 cm^{-1} in the TERS spectra, and its standard error value (STDEV) is 3.95 cm^{-1} , whereas the corresponding shift is only 2 cm^{-1} in the normal Raman spectra, and the STDEV is 0.84 cm^{-1} . For the G^+ peak, the largest shift is about 10 cm^{-1} for the TERS result, and the STDEV is 3.13 cm^{-1} , whereas it is about 2 cm^{-1} for the normal Raman result, and the STDEV is 0.99 cm^{-1} .

The G' band position was also compared between the far-field Raman and TERS spectra for each point. For the

FIG. 7. Raman and (b) TERS spectra in the region of 1700–1500 cm^{-1} of 0.5 wt.% SWCNT/PS nanocomposites measured at nine points. (From ref. [55].)

G' band, the largest shift is about 11 cm^{-1} in the TERS spectra, with 3.50 cm^{-1} STDEV, whereas it is 6 cm^{-1} in the normal Raman spectra, with 2.57 cm^{-1} STDEV. The shift behavior in the Raman bands of SWCNTs can arise from three possible mechanisms: chemical interaction between SWCNTs and the matrix, such as charge transfer or chemical bonds; changes in the tube-tube interactions due to the distribution of SWCNTs; and mechanical compression from the polymer matrix. In the normal Raman study of SWCNT/PS composites, Yan *et al.* [62] concluded that the shifts of the G and G' bands are due to the mechanical compression from PS matrix to SWCNTs. In detail, it means that the polymer matrix forms a compressive envelope around the nanotubes, and transfers the hydrostatic stress to CNTs. Therefore, CNTs would suffer shrinkage due to the hydrostatic stress from polymer. It is well-known that elongation or shrinkage of carbon atom vibrations causes shifts in Raman bands of CNTs by several wavenumbers. Here, the shrinkage from PA6 hydrostatic stress finally induces a higher shift in the Raman spectra.

The TERS study by Yan *et al.* [55] revealed that the G and G' bands in the TERS spectra show an obvious point-to-point dependent shift with a similar shift degree. According to previous studies [61], the G' band is more sensitive to the mechanical compression than the G band, and shifts by much larger degree than the G bands under compression. Thus, the G' band has been considered as a desirable indicator for mechanical compression. In the study by Yan *et al.* the shift of G' band indicated

FIG. 8. Point-dependent changes of wavenumber of G^- (a) and G^+ (b) bands in normal Raman spectra (solid square) and TERS spectra (solid circle). (From ref. [55].)

that mechanical compression from the PS matrix to SWCNTs varies in the local area from point to point. The disentanglement of CNTs and the penetration of a polymer into CNT bundles during melt mixing would cause a G band shift [63]. In the SWCNT/PS system, polymer chains penetrate into the bundle of SWCNTs at some points, while at other points, SWCNTs exist in aggregation states. This dispersion of SWCNTs in the PS matrix would induce a different effect on the molecular vibration of SWCNTs. Therefore, Yan *et al.* [55] concluded that the G band shift behavior in the TERS spectra is due to both the distribution of SWCNTs in the PS matrix and the point-dependent mechanical compression from the PS matrix, which has never been observed by confocal Raman measurements.

C. Tip-enhanced Raman spectroscopic measurement of stress change in the local domain of epitaxial graphene on the carbon face of 4H-SiC (0001)

Suzuki *et al.* [40] reported a TERS investigation of stress change in the local domain of epitaxial graphene on the carbon face of 4H-SiC (0001). Epitaxial graphene grown on SiC has been a matter of keen interest because of its large sheet area, minimal defects, and electrical insulation properties of SiC, which allow the application in electronic circuits without the need of substrate transfer processes [64, 65]. The face of SiC in which graphene is grown on does affect SiC-graphene in-

FIG. 9. Raman spectra of epitaxial graphene on the carbon surface of 4H-SiC (000 $\bar{1}$) measured under (a) tip-approaching conditions, and (b) tip-retracted conditions. (c) The difference spectrum calculated by subtracting spectrum (b) from spectrum (a) (TERS spectrum). (From ref. [40].)

FIG. 10. Enlarged Raman and TERS spectra in the 1750–1450 cm^{-1} region of epitaxial graphene on the carbon surface of 4H-SiC (000 $\bar{1}$) from Fig. 9. (From ref. [40].)

teraction. Graphene grown on C-face of SiC (000 $\bar{1}$ face) is much weakly attracted by SiC substrate compared to graphene grown on Si-face (0001 face). This allows some interesting features to occur in graphene on C-face, such as stack twisting of multilayer graphene, which allows extremely high mobility. The weak attraction also allows nanostructures, which alters physical and electronic properties, to be presented on the graphene sheet grown on C-face of SiC [66].

In the study by Suzuki *et al.* [40] the G band in the TERS spectra of epitaxial graphene on the C-face of 4H-SiC exhibits position-by-position changes in both lower wavenumber shifts and spectral broadening. The analysis of the changes revealed that the shifts and broadenings have a linear correlation between each other, indicating that the changes are induced by the position-dependent local stress on graphene based on a uniaxial strain model. A Raman spectrum in the 4500–1000 cm^{-1} region at a particular spot in epitaxial graphene on the 4H-SiC (000 $\bar{1}$) surface measured under tip-retracted conditions is shown in Fig. 9 [40]. Figures 9(a) and (b) depict spectra collected under tip-approaching and tip-retracted conditions. It is

FIG. 11. The plot of a correlation between the peak shift and the DFWHM of the G band at different positions. (From ref. [40].)

FIG. 12. Tip-attached, tip-retracted, and subtracted Raman spectra of C-face epitaxial graphene from area with single layer graphene. (From ref. [41].)

noted that signals at 2695 and 1584 cm^{-1} in Fig. 9(a) are enhanced strongly. Moreover, signals at 3246 and 2450 cm^{-1} become strong markedly, and those at 4282 and 2928 cm^{-1} , which do not appear or almost missing in Fig. 9(b), appear clearly in Fig. 9(a). The signals at 3246, 2928, and 2450 cm^{-1} are assigned to G'' (2LO), G + D, and G* (LA + iTO), respectively.

Figure 9(c) shows a TERS spectrum of epitaxial graphene on the 4H-SiC (000 $\bar{1}$) surface [40]. Of particular note in the TERS spectrum is that the signal-to-noise ratio is extremely high. The enhancement factor of the TERS spectrum in Fig. 9 is superior to those of any TERS spectra of graphene previously reported. The enhancement factor of the TERS spectrum was estimated to be about 1000 using the ratio between the area of near-field Raman detection and that of the far-field one (1:180) and a total signal enhancement of 640%.

It is noted that the G band of the TERS spectrum shows a lower wavenumber shift by 12 cm^{-1} from that of the Raman spectrum (see Figs. 9(b) and (c)) [40]. The enlarged spectra in the G band region (the 1750–1450 cm^{-1}

FIG. 13. TERS measurement on step structure. (a) AFM topography image and line height profile. (b) G' band in far-field Raman and TERS spectra from five measurement points shown in (a). (c) Peak position of each G' band in (b), plotted against distances from point 1 along the line profile in (a). Error bars in (c) were calculated from uncertainties in Lorentzian fitting. Some errors bars are too small to be clearly visible. (From ref. [41].)

region) for the Raman and TERS spectra in Fig. 9 are depicted in Fig. 10. The comparison of the G band in the TERS spectrum with that in the Raman spectrum revealed a change in the band width as well as that in the band shift. It was found from the curve fitting that, the full width at half maximum (FWHM) changes from 14 to 24 cm^{-1} upon going from the Raman spectrum to the TERS spectrum. It seems that the large change in the band width is due to the fact that the spatial resolution of TERS is much higher than that of normal Raman scattering, and TERS observes much smaller area. The spatial resolution of the TERS spectrum was 75 nm. Thus, the differences between the TERS and Raman spectra may arise from changes in the fine structure and local conditions. The G band width for TERS is broader than that for normal Raman, indicating that the result is not due to common inhomogeneous broadening, but due to some local properties which is negligible for normal Raman.

Suzuki *et al.* [40] measured position-dependent TERS spectra of graphene and found that the peak shift of the G band and the change in its FWHM are different from place to place. Figure 11 plots the difference in the G-bandwidth between the normal Raman and the TERS spectra (ΔFWHM) versus the peak shift of the G-band [40]. As the absolute value of the peak shift of the G band becomes larger in the TERS spectrum, its ΔFWHM increases. Previous Raman studies of graphene suggested that the G band shift and broadening are mainly induced by two kinds of perturbations; hole and electron doping and stress on graphene. G band shifts and changes in the FWHM have been observed by doping holes and electrons by applying the voltage to graphene [64, 65]. The first possibility was excluded by Suzuki *et al.* [40] and they focused on the stress on graphene as the origin of the G band shifts and broadening. In the SiC thermal decomposition method, graphene underwent through thermal expansion. The coefficient of thermal expansion of the graphene layer ($-9 \times 10^{-6} \text{ K}^{-1}$) [66] is different from that of the SiC substrate ($4 \times 10^{-6} \text{ K}^{-1}$) [67], inducing the difference that generates thermal stress between SiC and graphene during a cooling process of graphene just after its fabrica-

tion. When unidirectional stress is applied mechanically to graphene, the G band is split into two directions where the stress is applied and not applied, yielding the G^+ and G^- bands [68]. When the stress is weak, the splitting of the G band is small and looks broadened. It was reported that the G band shift upon applying the stress to graphene because of the distortion of the graphene lattice [69].

In the preparation conditions of graphene of the study by Suzuki *et al.* [40] ridge structures were commonly observed in AFM images. The graphene at the ridge part is somewhat away from the substrate, and thus distortion of the graphene lattice is significantly different from that at the flat part. The graphene surface has a wide flat area (about several mm) and a very small ridge structure area. In the normal Raman spectra, the signal from the flat area is dominant, while the signal from the ridge structure should be observed in the TERS spectra. Thus, Suzuki *et al.* [40] considered that variations in the local stress at ridge structures are the origin of the observed variations in the G band. They carried out the TERS experiment in a noncontact mode, and thus, the effect of the force from the tip seemed to be negligible. The degree of the G band shift and broadening shows position-by-position variations. Therefore, the variations are likely induced by the position-dependent stress at the ridge structures generated during the fabrication of epitaxial graphene on the C-face. This band shift due to the presence of ridge structure was later proofed by Vantasin *et al.* [41], which will be further elaborate in next section.

D. Tip-enhanced Raman Scattering of the Local Nanostructure of Epitaxial Graphene Grown on 4H-SiC (000 $\bar{1}$)

Vantasin *et al.* [41] performed a TERS study on local nanostructures of epitaxial graphene grown on 4H-SiC. They characterized step, ridge, and crack sub-micro/nanostructures of epitaxial graphene on 4H-SiC (000 $\bar{1}$) by correlating TERS spectra with AFM images. As explained in the previous section, these nanostructures

FIG. 14. TERS measurement on ridge structure. (a) AFM topography image and line height profile. (b) G' band in far-field Raman and TERS spectra from seven measurement points shown in (a). (c) Peak position of each G' band in (b), plotted against distances from point 1 along the line profile in (a). (d), (e) Calculated relative uniaxial and biaxial strain on each point, plot in the same fashion as (c), respectively. Error bars in (c), (d), and (e) were calculated from uncertainties in Lorentzian fitting and Grüneisen parameter. (From ref. [41].)

were generated in the cooling process from synthesis temperature due to the difference in thermal expansion coefficient between graphene and SiC. This TERS study found the effect of nanoridge on the local strain of graphene by analyzing the G' band position. The strain on the ridge was calculated to be 1.6×10^{-3} assuming uniaxial strain model. The graphene content in the sub-micrometer crack also found to be much lower compared to nearby areas. This study demonstrates the advantage of TERS over conventional Raman spectroscopy in which exceptional spatial resolution allows characterization of each individual nanostructure.

Figure 12 depicts tip-attached, tip-retracted, and subtracted (TERS) spectra of single-layer epitaxial graphene on the C-face of SiC [41]. The spectra in Fig. 12 show characteristic features of single layer graphene such as G' band being more intense than G band and FWHM of the G' band lower than 27 cm^{-1} (in this case, 23 cm^{-1} for TERS spectra) [41]. Actually, the actual sample has 1.7 layers of graphene on average but every spectrum in the study was measured from single layer areas to eliminate the layers effect. Interestingly, this sample has extremely low defect, as denoted by the missing of the D band in the 1350 cm^{-1} region.

Figure 13(a) depicts an AFM image of step structure of graphene [41]. The step nanostructure characterized in the study was shown to not affect TERS spectra (Figs. 13(b) and (c)), and thus has no effect on mechanical strain and electrical doping. The reason is that the 2 nm step height came from the inherent step of under-

lying SiC. Therefore, the graphene itself is mostly unaltered. The IG/IG' ratios and small FWHM of G' band confirm that the step is not the difference in number of layers, since every point measured indicates single layer graphene.

As explained above, in the cooling from the synthesis, SiC shrank more than graphene due to the difference in thermal expansion coefficient. This exerted compressive strain on graphene. However, being a two dimensional material, graphene can be pushed out of plane into a ridge when the generated strain exceeds a limit called critical buckling strain. The presence of buffer layer on C-face of SiC also plays a role in this process, since it reduces the attraction between graphene and SiC. Figure 14(a) shows an AFM image of the ridge structure. Figure 14(b) shows that G' band position in TERS spectra from the ridge center is reduced by 8.7 cm^{-1} in relative to the reference TERS spectra from flat area. It is certain that this shift is not due to the tip interaction because the tip was controlled by non-contact mode. Therefore, the shift must come from the deformation cause by the ridge.

Even though the downshift of G' band usually denotes a stretching (tensile) strain, due to decreased phonon frequency from bond lengthening [70, 71], the G' band position in the TERS spectra from the ridge, at 2691 cm^{-1} , is still far higher than the band position of 2674 cm^{-1} from unstrained and undoped graphene [72, 73]. This means the shift of G' band from the ridge is actually a smaller compressive strain compared to neighbor area, not

a stretching strain.

By using data in Figs. 14(c), (d) and (e) to do the comparison between TERS and normal (far-field) Raman spectra, another interesting information could be interpreted. Since TERS probes small area around the tip while far-field Raman spectroscopy probes much larger area, and in every point the G' band positions in TERS spectra are lower, it means that the even the flat areas around the ridge also has weaker compressive strain in relative to areas far from the ridge. The ridge itself, without a doubt, has weakest compressive strain since the difference in G' band between near-field and far-field spectra on the ridge is as high as 11.1 cm^{-1} .

Vantasin *et al.* [41] also explored crack sub-microstructure using TERS. The TERS spectra of the crack structure showed a reduced graphene/SiC signal ratio, which cannot be probed by far-field Raman spectroscopy. These results of step, ridge, and crack structures of epitaxial graphene suggested that TERS is an excellent tool in the characterization of nanostructures on epitaxial graphene.

III. CONCLUSIONS

This review paper reported recent progress in TERS studies of polymer nanocomposites and graphenes. We were able to demonstrate that TERS is powerful in investigating local structure and interaction of nanomaterials with a special resolution of 10–100 nm. TERS has provided new insights into the nature of the intermolecular interactions and interface structure of polymer nanocomposites. TERS may open a new avenue for investigating polymer nanomaterials interfaces.

To develop further TERS studies of graphenes one needs a standard graphene sample that is high quality graphene with few defects and a definite number of layers. Recently, in general, the quality of graphenes has become much better than before, and thus one can establish TERS spectra of standard graphene. By using the standard graphene it is important to develop general TERS methods of characterizing graphenes; for ex-

ample, a method for determining the number of layers of graphene.

As new techniques in this research field both TERS imaging and TERS measurement under ultra-low temperature and ultra-high vacuum have recently been matters of keen interest. The former is still under development and currently mapping techniques are widely used. If the TERS imaging technology would develop further, TERS characterization of nanomaterials would become much easier and faster, providing popular spectroscopic analysis method for nanoscience and technology. TERS instruments that are used under ultra-low temperature and ultra-high vacuum are also under progress. Under these environments samples are very stable and free from dusts, so that TERS measurements under these environments should yield very high quality TERS spectra. Molecular structure and molecular interaction may also change under ultra-low temperature and ultra-high vacuum.

At last but not at least, we would like to point out that one of the key technologies in TERS which have serious problems is TERS tips. The sensitivity and special resolution of TERS spectra highly depend on the quality and TERS tips. However, still it is not easy to produce the high quality TERS tips steadily. It is highly desirable to investigate the shape, size, and materials of high quality TERS tips experimentally and theoretically.

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