NEW RAMAN FEATURE AND NATURE OF LOW-DIMENSIONAL AND NANO-SCALE SEMICONDUCTORS

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Abstract: Raman spectroscopy of low-dimensional and nano-scale semiconductors, including their intrinsic Raman spectra, their implications on the fundamental Raman principle and application theory are discussed.

It is well known that every object has its own unique intrinsic Raman spectrum (IRS), which is why Raman spectroscopy is often considered a fingerprinting technique. The identification and application of IRS is a major aspect of Raman spectroscopy.

The Raman spectral theory is another major aspect of Raman spectroscopy. There are two components: the fundamental principle and application theory. There are two universal dependencies of the Raman frequency (UDRF) in the fundamental principle: the Raman frequency is independent of excitation wavelength (UDRF1) and the absolute frequency shift of the Stokes peak is identical to that of the corresponding anti-Stokes peak (UDRF2). Application theory refers to the many practical models used to interpret various Raman features.

In retrospect, the development of Raman spectroscopy is based on uniform three-dimensional (3D) and large-scale (LS) objects. Therefore it is often predicted that new Raman phenomena may appear and that the current Raman principle may be challenged when low-dimensional (LD) and nano-scale (nano) materials are studied. As a result, current understanding of Raman spectroscopy may need to be modified and further developed.

Intrinsic Raman spectrum (IRS)

- Nano-nonpolar semiconductors

Due to the presence of significant amount of impurities and/or the weak Raman signal, using IRS to identify nano-materials (NMs) can often lead to error, such as in the case of porous Si (PS) and nano-crystalline diamond (NCD) [1-3]. The correct IRS of nano-nonpolar semiconductor PS [4], Si nano-wires (NWs) [5] and NCD are shown in Figs 1, 2, and 3, respectively. All three IRS have similar Raman features, e.g. in terms of the frequency shift, the linewidth broadening and the
lineshape asymmetry, which are different from those of the corresponding bulk materials.

The solid line spectra in Fig 1 and Fig 2 are the theoretical Raman spectra calculated by the micro-crystal model (MCM). The good fit between experimental and theoretical spectra indicates that nano-nonpolar semiconductor essentially maintains its crystalline nature. Based on calculations using the bond susceptibility model (BSM), the theoretical spectra of Si nano-wires with different diameters (in unit of lattice constant a) is shown in Fig 4. These theoretical Raman spectra consist of discrete peaks, in sharp contrast with the experimental spectra (Fig 1 and 2). The spectrum in the bottom panel of Fig 5 is the superposition of the theoretical spectra in Figure 4 with different weighting factors for different diameters. Comparing the theoretical spectrum with the experimental one (shown in the top panel of Fig 5), we may conclude that the Raman spectrum of nano-materials is made up of discrete peak contributions, resembling those from the discrete line-like Raman spectrum of atoms. In other words, if the sample consists of a single size rather than a collection of different sizes, we would expect to observe line-like spectrum in nano-materials.

- **Nano polar semiconductors**

Fig 6 and Fig 7 show the Raman spectra of typical nano polar semiconductors, GaN NWs and SiC nano-rods, respectively. The spectra cannot be adequately fitted using the MCM. We notice that these spectra are very similar to those of their corresponding amorphous materials, as shown in Fig 6 (b), for example. The calculated spectrum using the amorphous crystal model (ACM) fits the experimental spectrum well, as shown in Fig 7 (b) [6]. The above results show that nano polar materials can possess amorphous property although they may look crystalline in X-ray measurement. This dual aspect of crystalline and amorphous features of nano polar materials is new and is hard to imagine traditionally.

Concerning the origin of this dual property, we think it may be due to the long-range Coulomb (Fröhlich) interaction that exists only in the polar semiconductors.

**Dependence of Raman frequency on excitation wavelength**

- **Nano-nonpolar semiconductors**

Abnormal UDRS1 phenomenon was first revealed in carbon nanotubes (CNTs) [7] and then in Si NWs [8]. Rao et al attributed this phenomenon to diameter-selective Raman scattering (DSRS). They calculated the dependence of the electron density of states (DOS) on energy and the dependence of phonon frequencies on excitation wavelength for various CNT with different index
(m, n), i.e., different tube diameter to support the DSRS interpretation. Based on the DSRS mechanism, for two with different size distributions but with the same dominant size, one expects that, depending on whether the exciting laser energy is at or out of resonant, the corresponding spectra will either have the same or different Raman spectral features. The experimental results of two such Si NW samples, C and D, shown in Fig 8 and 9, confirm this prediction. It suggests that the abnormal UDRS1 originates from the size confinement effect coupled with a different size distribution of samples. This result also indicates that if the sample consists of a single/uniform size, there will be no abnormal UDRS1. Therefore, UDRS1 does not violate the fundamental principle of Raman scattering.

- **Nano polar semiconductors**

In the nano-crystalline polar semiconductors SiC NRs, GaN NWs and ZnO Nano-tubes (NTs), we did not observe the abnormal UDRS1, as shown in Fig 10 (a), (b) and (c), respectively. Note that the Raman scattering of polar nano-semiconductors possesses the amorphous scattering feature, where there is no correlation between the phonon DOS and the size. The above result should be expected. This gives further confirmation on the amorphous nature of nano polar materials.

![Raman Spectra at Resonance of Si NW Samples C and D](image1)
![Raman Spectra Out of Resonance of Si NW Samples C and D](image2)

Fig 8 Raman spectra at resonance of Si NW samples C and D.

Fig 9 Raman spectra out of resonance of Si NW samples C and D.

![Raman Spectra at Resonance of SiC NRs](image3)
![Raman Spectra Out of Resonance of SiC NRs](image4)

Fig 10 Dependence of Raman frequency with incident wavelength for SiC NRs (a), GaN NWs (b) and ZnO NTs (c).

**Absolute frequency shift of the Stokes and the corresponding anti-Stokes Raman peak**

The abnormal UDRS2 was observed in the D mode of CNTs unambiguously (see Fig11), as this abnormality is independent of changes in excitation wavelength, sample temperature, wall number and semiconducting versus metallic property of CNTs [9].

The nano-tubular structure of CNTs can be considered to be a defected (rolled-up) structure as compared to the flat graphite sheet. Thus, the degree of defect can be expressed by the tube diameter $d$, with the limit $d \to \infty$ corresponding to the (non-defective) flat graphite sheet.

We attributed this abnormality to the defect of CNT structure itself. If this interpretation is correct, the abnormality, $\Delta = 1 \omega_s - 1 \omega_{as}$ ($\omega_s$ and $\omega_{as}$ are the frequency of Stokes and anti-Stokes peak, respectively), should decrease with increasing $d$. Fig 12 shows the observed dependence of $\Delta$ on the average diameter $<d>$ of two samples. The result shown in Fig 12 confirms that abnormal
UDRS2 originates from the global nano-scale tubular structure of CNTs itself and is just a special case in defect/impurity containing systems.

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