Phonon Confinement in Germanium Nanowires

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Abstract: Raman spectra for different size Ge nanowires were measured with different excitation laser powers and wavelengths. By eliminating the heating of the sample under illumination, the phonon confinement effect for small size nanowires was clearly identified.

One-dimensional crystalline structures such as nanowires and nanotubes have been studied extensively during the past several years. Semi-conducting nanowires promise applications in future generation electronic and optoelectronic devices. Raman microscopy is a useful tool in the study of quasi-1D materials; it provides information about the surface and volume phonon modes and lattice vibrations, including how those vibrations are affected by extreme small dimensions. Recently, several papers [1, 9, 10] have analyzed the Raman peak shifts and the shape of the Raman spectrum for Si nanowires. However, the reported shifts and asymmetric broadenings vary depending on the experimental conditions. Studies show that the optical phonon peaks of Silicon nanowires are dependant on the excitation laser power and independent of wavelength. Thus low laser power is essential in order to examine the phonon spectrum of different size nanowires [1].

Self-assembled single crystalline Germanium nanowires can allow researchers to observe relatively strong one-dimensional confinement effects for both carriers and phonons. Compared to Si, Ge has smaller electron and hole effective masses and a lower dielectric constant; therefore, nanowires made of Ge should have stronger confinement characteristics than Si nanowires with the same diameters.

The samples considered in this paper were synthesized on lithographically patterned Au catalyst arrays, with sizes ranging from 5nm to 20 nm, by the Vapor-Liquid-Solid (VLS) method. The details of the process can be found in Ref [2]. As a reference, a piece of bulk Germanium wafer was also examined under same conditions. The ambient temperature was kept at typical room temperature, 22ºC. Raman spectra for different size Ge nanowires were measured with different excitation laser powers and wavelengths. By eliminating the heating of the sample under illumination, the phonon confinement effect for small size nanowires can clearly be identified. Fig. 1 shows the scanning electron microscopy (SEM) images of the as-synthesized germanium nanowire.

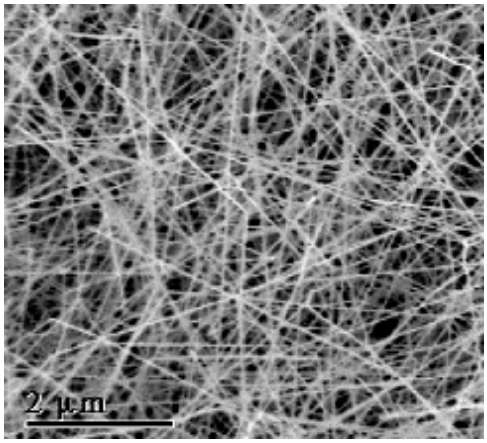

Fig.1 A SEM image of as-synthesized GeNW sample.

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Fig. 2 shows the evolution of Raman spectrum as a function of wire diameter. All the four samples were excited by 514.532nm, 500 μW Kr^+ laser line and examined the scattering light. We are mainly interested in the Strokes peaks in the Ge range (~300 cm^{-1}). Comparing these to the Strokes peak of bulk Ge, we observed obvious position shift-downs, broadenings and increases of asymmetry from GeNWs. As the wire size decreases, these features become more significant. Earlier paper [8] reported these phenomena as a entire contribution of scaling- induced phonon confinement effect. However, the pure confinement effect should be looked at only after carefully calibrating and removing the environmental contributions. In this experiment, we kept the ambient temperature stable and the excitation times for each measurement equal. We also used a clean room for taking measurements in order to reduce contaminations. But localized heating at the excite point can not be totally eliminated, since this is inevitable when focusing extreme small targets with lasers.

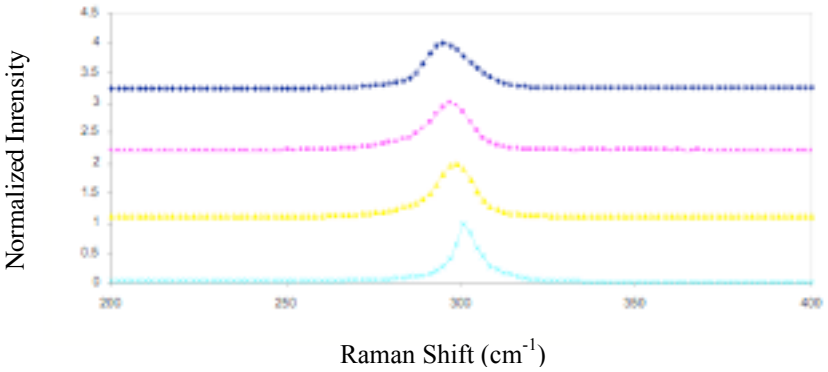

Fig.2 Typical evolution of Raman spectrum as a function of wire diameter.

In order to separate the influence of local heating from that of the pure phonon confinement, we took another set of Raman spectrums on these four samples. All experimental conditions and parameters were kept the same, except the excitation laser power was reduced to a very low level, 50 μW . Results are shown in Fig. 3(A). The spectrums obtained with the 500 μW excitation were superimposed and shown in Fig. 3(B). Comparing Fig. 3 (A) with (B), we clearly obtained much smaller $|\Delta shift/\Delta size|$, and $|\Delta broadening/\Delta size|$ ratios.

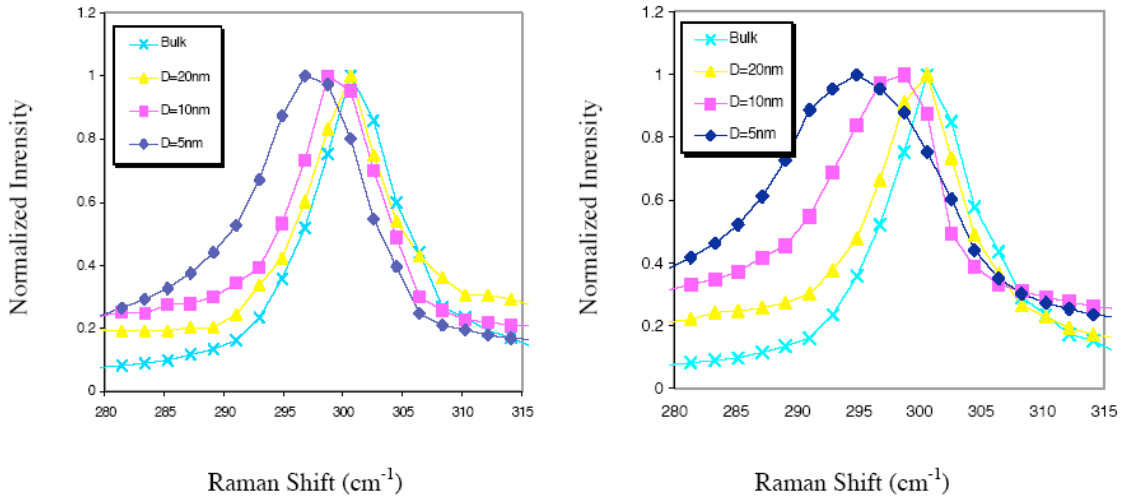

Fig.3 (A) Different size GeNWs' Raman Strokes peak at low excitation power;
(B) Different size GeNWs' Raman Strokes peak at high excitation power;

To further understand how the local heating affects Raman spectra, each of the differently sized Ge nanowire samples was excited by three different laser powers. See Fig. 4 (A-C). Neutral Density Filters (NSFs) were added in-between the sample and laser source to indicate the different excitation powers. From a $500\,\mu W$ source, the D0, D0.3 and D0.6 filters, allow, respectively, $500\,\mu W$, $250\,\mu W$ and $125\,\mu W$ laser powers to pass through. As the power increases, the Raman Strokes peaks of GeNWs generally move to lower frequencies, broaden and become less symmetric, while no significant change can be observed from those of the bulk Ge. This is consistent with what has been found for Si and Si nanowires [1]. Another interesting find is the difference between changing speeds of differently sized wires. Thinner wires respond to excitation power change much more obviously than thicker ones. This trend is valid for all different size nanowire samples, until there is no local heating effect, as approximately what happens with the bulk material.

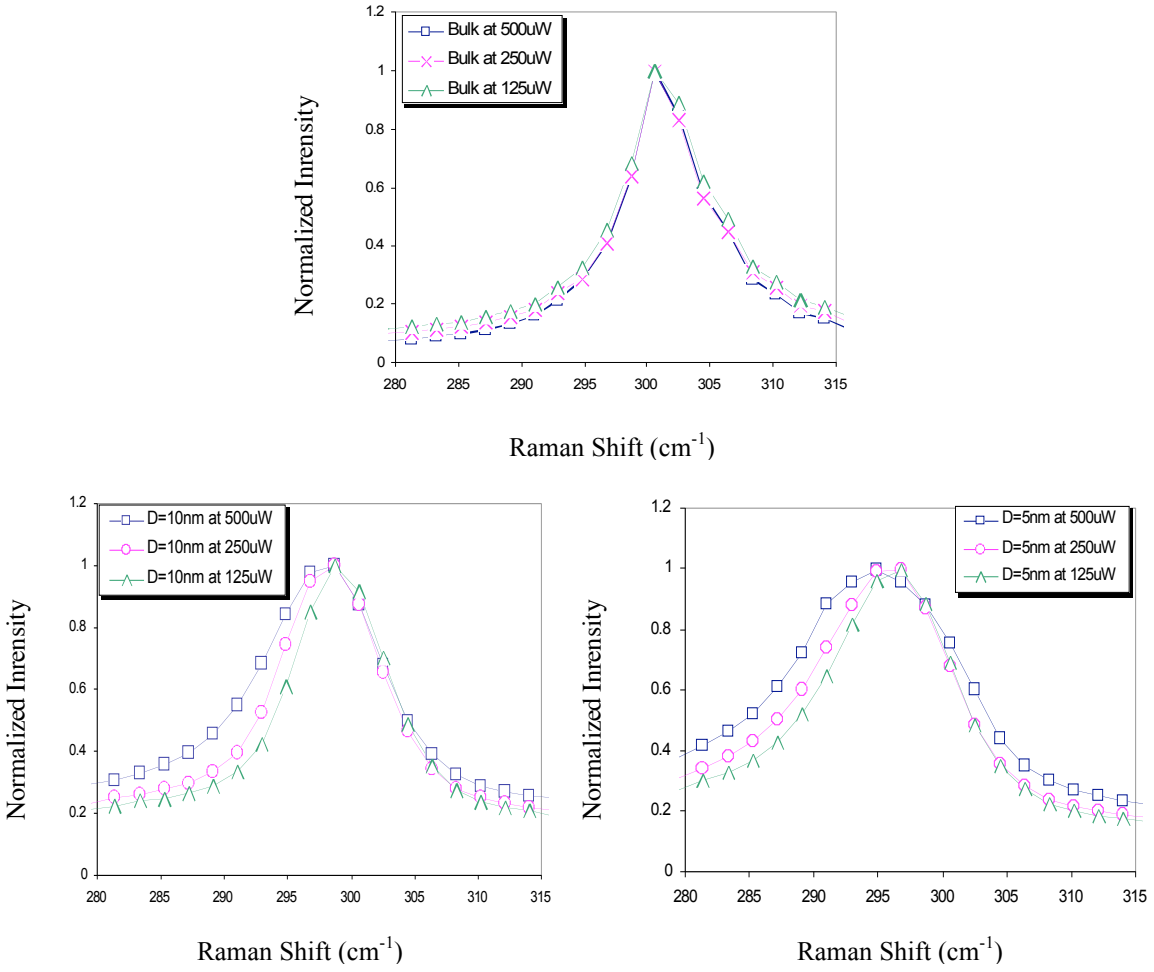

Fig. 4 (A) Raman Strokes peak of bulk Ge with different excitation powers;
(B) Raman Strokes peak of 10nm GeNWs with different excitation powers;
(C) Raman Strokes peak of 5nm GeNWs with different excitation powers;

A quantitative analysis can help us distinguish the scaling-induced phonon confinement effect from the gross. Take the spectra of 5nm size GeNW as an example: if the downshift at low power excitation, ~3.1cm^{-1}, is considered as a pure local heating contribution, the downshift accompanying the higher power excitations can be estimated by doing a first order approximation and should be very close to the measurement value. To estimate the Strokes peak downshift with high power excitation, with calculated the

ratios between magnitudes of Stokes and Anti-Stokes peaks. $I_{AS}/I_S = \gamma \exp(k_B T/h\nu)$, where T is the local temperature, ν is phonon energy and γ is a coefficient relates to peak position and FWHM. [11, 12, 13]. We found out that the local temperature range is 305-380K, as the power varied from 50uW~250uW. Then, as a rule of thumb, for the 5.6cm^{-1} downshift excited by 500μW power, a local heating of ~440K should be found in the case of excluding all other contributions rather than local heating. S. Piscanec *et al.* have used the similar method in their study of Si nanowires [1]. However, only 405K was found based on the peak features. It is much smaller. The only issue that may cause inaccuracy in this approximation is that the shape of the peaks could not be perfectly fitted by ideal Lorentzian pulses. After investigation, the Least-Mean-Square fitting error was found only gives less than 5% of the intensity ratio difference and less than 0.1cm^{-1} of the position variance, which respond to downshift uncertainties of ~0.35% and ~0.5%, respectively. Therefore, we are confident of the participation of optical phonon confinement.

The small physical dimension of the scattering crystalline nanowire leads to downshifts and broadening of the first –order Raman line, known as the scaling-induced phonon confinement effect. More specifically, in one-dimensional structures, such as nanowires, a zero momentum exists along the axis directions, and phonons with momentums close to the Brillouin zone center allow the Raman scattering to occur at 300.6 cm^{-1}. However, in directions perpendicular to the axis of the wire, momentum level is discrete and spaced by $2\pi/d$, where d is the physical dimension and indicates the size effect. When phonon modes are confined, the degeneration of longitudinal optical mode (LO) and transversal optical mode (TO) disappears, while the momentum k=0 in infinite structures allows the degeneration to exist. This causes the general broadening. In this study, different speeds of shifting and broadening as a function of excitation power for different size wires are considered the results of the size distribution of wires on each sample. Although the size of catalysts can control the size of synthesized nanowires, a slight variance of the wire size is inevitable due to the nature of self-assembling growth. For instance, if the sizes of wires range from 4nm to 6nm, averaged and centered at a catalyst size, 5nm; while another set of wires has a size distribution from 9nm to 11nm, centered at 10nm, then both of the samples have an internal variation $\Delta d = \pm 1nm$. However, the same size variations that exist in different samples do not exhibit the same changes. More specifically, it broadens the shape and shifts the central position of the Raman peaks more with thinner wires, while less with thicker wires. The local heating enlarges this phenomenon, since the thermal conductivity of semiconductor nanowires is more than approximately two orders of magnitude lower than the bulk value and it decreases as the size scales down [3]. The laser power more easily accumulates in thin nanowires.

As a supplemental study, two different excitation laser lines: a 514.523 nm Ar^+ laser line and a 633.817 nm Kr^+ laser line, were used on all four samples to examine the wavelength independency. Fig. 5 (A-B) shows these results. Power used for both of the laser lines were 500uW. The absorption coefficients of Germanium are 600 cm^{-1} for Ar^+ laser and 150cm^{-1} for Kr^+ laser. Therefore, with the different absorption coefficients the excitation powers match what have been used above: 125μW (Kr^+) and 500uW (Ar^+). Comparing these spectra to Fig. 4 (B, C), features of spectrums—position, FWHM, and asymmetry level—almost stay the same. In other words, the spectrum changes with the different wavelengths used are not due to resonant Raman selection of different size wires, but the results from the absorbed power difference.

In conclusion, we showed that the Raman spectra for different size Ge nanowires were measured with different excitation laser powers and wavelengths. Study shows the excitation power dependency and wavelength independency of Raman spectrum evolution. By eliminating the heating of the sample under illumination, we can clearly identify the phonon confinement effect for small size nanowires.

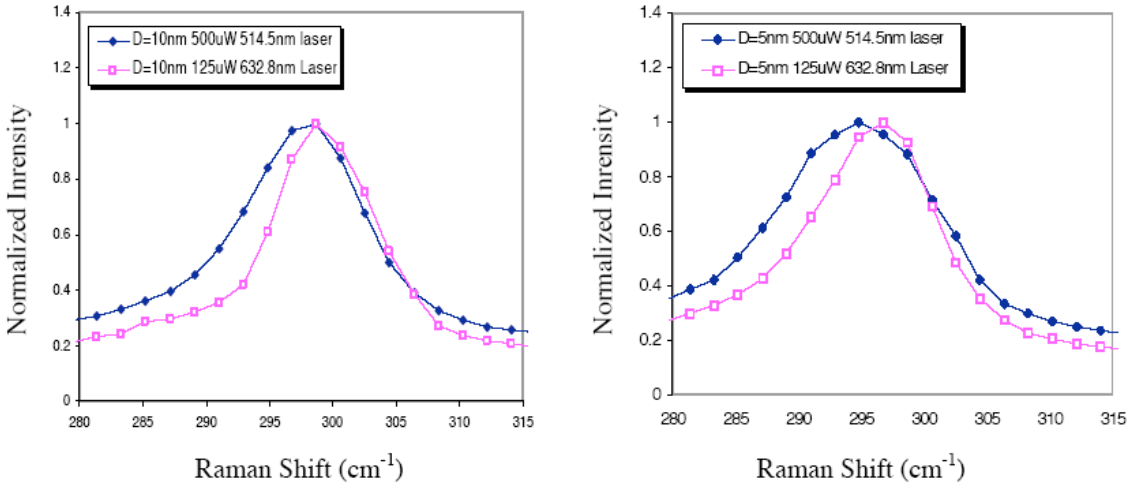

Fig. 5(A) Raman Strokes peak of 10nm GeNWs with different excitation wavelength;
(B) Raman Strokes peak of 5nm GeNWs with different excitation wavelength;

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