Supporting Information

Amplification or Cancellation of Fano Resonance and Quantum Confinement Induced Asymmetries in Raman Line-Shapes

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A short discussion on Equation 1 in manuscript

Generalized theoretical equation to represent Raman line-shape obtained from poly (nano)-crystalline silicon has been given by Richter et al[1] and later modified by campbell *et al.* [2] which shows the effect of finite crystallite size on the Raman selection rule criteria and the Raman line-shape. The equation can be represented as follows:

$$I(\omega) = \int_0^1 F(k)C(k)d^n k \qquad \text{(S1)}$$

Where $F(k) = \frac{1}{\{[\omega-\omega(k)]^2+(\frac{\Gamma}{2})^2\}}$ is a general Raman line-shape function obtained by considering the effect of phonons in the crystal that lie away from the zone center. where Γ is the full width half maximum of Raman line shape of crystalline semiconductor and $\omega(k)$ is the dispersion relation (can be optical or acoustic) of particular system/material, 'n' being the degree of confinement and $C(k)$ is the weighing function that may vary according to size, shape and type of confinement. $C(k)$ is also the measure of the relative contribution of a phonon corresponding to a given 'k'. The detailed interpretation has been given by *Kumar et al.* elsewhere[3]. The typical Lorentzian Raman line-shape obtained due to only zone center phonon can be written as $\frac{1}{\{[\omega-\omega(0)]^2+(\frac{\Gamma}{2})^2\}}$ where ω(0) is the frequency of zone center phonon. Apart from the analytical derivation of Eq.S1 as reported by above-mentioned researchers, an alternate method to obtain the same equation by logical replacement/substitution of terms in Eq. S1 is possible as reported elsewhere[3]. To extend the scope of Eq. S1 further modification in term $F(k)$ can be done. $F(k)$ of following form, earlier proposed by U. Fano[4], makes the equation more general by incorporating e-phonon (Fano resonance) interaction term in addition to the size effect:

$F(k) = \frac{(\varepsilon+q)^2}{(1+\varepsilon^2)}$, $\varepsilon = \frac{\{\omega-\omega(k)\}}{0.5\Gamma}$ q is Fano parameter. Equation S1 will take the following form after the abovementioned replacement for a two-dimensional (n=2) confinement:

$$I(\omega) = \int_0^1 \left[\frac{(\varepsilon+q)^2}{(1+\varepsilon)}\right] C(k) d^2k, \qquad \text{(S2)}$$

It is also important to mention here that Eq. S2 represents Raman line-shape for a system having only quantum confinement effect in the limiting case of q = ∞. Equation S2 is also a very widely used equation for explaining experimental Raman data for appropriate systems[5–7].

Since there is no fundamental restriction on the use of Eq. S1 and S2, it can be used for acoustic phonons by appropriate modifications in phonon dispersion relation and weighting functions. The appropriate weighting function $C(k) = e^{-\frac{k^2L^2}{4a^2}}$ is being used to fit the experimental Raman data where L and "a" are the size and lattice parameter of semiconductor material both are having same unit of length. k is expressed in units of $2\pi/a$

Therefore the final equation become

$$I(\omega) \propto \int_0^1 \exp(-k^2L^2/4a^2) \left\{\frac{(\varepsilon+q)^2}{1+\varepsilon^2}\right\} d^2k, \quad \text{(S3)}$$

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