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Anharmonic interactions and temperature effects in Raman spectra of Si nanostructures

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ABSTRACT

An additional Raman phonon band observed for Si crystallites at high excitation power is studied theoretically. Laser-induced heating is supposed to induce stress in crystallites, leading to splitting of degenerated F_{2g}, E_g phonon states into A′ and A″ ones. The enhancement of anharmonicity effects expected at high temperature may lead to strong coupling between A′ (A″) fundamental modes with combination tones arising at splitting F_{2g}, E_g states. As a result, the Fermi resonance interaction between the optical modes from Γ-point and sum of acoustic modes from L-point can explain the temperature behavior of experimentally observed additional optical phonon band in Raman spectra of Si nanocrystallites.

1. Introduction

Raman spectroscopy is an efficient method of investigating semiconductor nanostructures, which allows one to distinguish between solid and amorphous state, to determine the phase or polytype composition, and to estimate the nanocrystal (NC) size and strain inside NCs [1]. Among most informative Raman features are those due to the first order scattering on optical phonons. For an unstrained bulk Si crystal of diamond structure a single optical phonons Raman peak is observed at $\sim 520\,cm^{-1}$ which corresponds to a triply degenerated optical F_{2g}-mode from the center of Brillouin zone. For NCs smaller that approximately 10 nm this feature is usually observed to broaden and shift to lower frequencies due to contribution of phonons with non-zero wavevectors [1].

The effect of temperature on the Raman spectra of silicon nanostructures is intensively discussed in the past years in the literature, because the frequency position and lineshape of the Raman peaks depend not only on the parameters of the nanostructures but also on the anharmonic effects [2–8]. When exciting the Raman spectra of Si NCs with a high laser power, Faraci et al. [2] observed two features instead of one near $520\,cm^{-1}$ which is commonly observed at moderate laser power. The most probable origin of the additional (lower-frequency) Raman peak was assigned in [2] to vibrations of NC surface atoms, enhanced due to "superheating" of the NC surface. The higher frequency peak was assigned to vibrations of the "bulk" atoms inside the NCs. In Ref. [3] the influence of exciting laser light of various powers was studied for Si NCs in the case of their good and bad thermal contact with a substrate. For NCs with bad thermal contact to the substrate, the downward shift of the phonon peak was larger.

The additional Raman bands in the range of main optical phonon peak have been also observed in some studies of bulk Si. In particular, in Refs. [9,10] peaks with frequencies noticeably different from $520\,cm^{-1}$ were observed upon phase transition of cubic diamond Si into hexagonal polytypes induced by nanoindentation.

Publications on Si nanowhiskers [11–14] also reveal two and more Raman bands in the range of optical phonons. The additional bands were explained by inclusions of hexagonal Si [11–13]. Note that for this kind of one-dimensional nano- and microstructures the crystal symmetry is different from that in 2D or 3D. Furthermore, for a large portion of atoms which are on the surface or close to it the force constants are different from that in the "bulk" of the whisker. The difference in force constants (or heat contact between micro- and nano-crystallite) can give rise to significant stresses which will manifest itself in Raman spectrum. The problem of stress in Raman spectroscopy and in particular in micro-Raman spectroscopy (MRS) of crystals has been discussed near thirty years [15] and was connected with study of vibration states having different levels of degeneracy. The most full theoretical aspects of influence of stress on the vibration spectra of Si crystal were considered in

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[16] where the new approach to analyze crystal surface stress by using the MRS was proposed. Authors note that MRS stress technique is very sensitive to the stress state and the lattice orientation of the crystal in the scatter volume. For example in work [17] it was shown that uniaxial loading of Si cube along ⟨100⟩ or ⟨111⟩ directions causes the initially triply degenerate F_{2g} mode in silicon to split into a singlet and doublet which can be observed independently. Both, singlet and doublet shift by different amounts with the applied stress. That as will be shown later is not so surprising, because arising doublet takes part in a new type of anharmonicity interaction, Fermi resonance (FR). Similar splitting F_{2g} mode on singlet–doublet was also observed in [18]. In work [16] it is also noted that in shear loading of Si-crystal in the ⟨110⟩ direction on the (111) plane the initially triply degenerate F_{2g} mode splits into three singlet *overlapping* peaks that cannot be isolated under any polarization conditions. For studies in the present work nano-crystal structures having irregular shape the situation, when full splitting of F_{2g} mode occurs, should be the most probable.

In present work, the effect of the thermal heating of Si NCs by high laser power onto their Raman spectra is studied theoretically by taking into account the effects of anharmonicity and Fermi resonance that can take place due to special structure of phonon bands of Si. One can notice that at strong heating of micro- and especially of nano-crystals (nano-whiskers) the effects of phonon anharmonicity will be enhanced and will have an influence on parameters of the Raman bands.

An alternative origin of the experimentally observed doublet structure in the first order Raman spectrum is proposed.

2. Model

The additional peak on the low-frequency side of bulk optical phonon at 520 cm^{-1} (peak I), which was observed at high laser power previously [2] and in this work, will be further referred to as peak II. This peak can be related with difference in heating of crystallites of different sizes, namely of nano- and micro-crystallites (also in Ref. [2]).

Two cases are possible for the latter hypothesis: (i) NCs are separated from the microcrystal (or film or other substrate) and (ii) NCs are a part of the microcrystal (as a nanoroughness, nanoprotrusion on the surface). In case (i), due to poor heat dissipation from NCs, the NCs can be heated by the laser beam up to much higher temperatures than microcrystal. As a result, the NCs will give the low frequency Raman band (peak II) and the microcrystals (films) – the bulk-like high-frequency band (peak I).

In case (ii), another mechanism of the appearance of doublet structure can be suggested. The difference in the temperature between NC and microcrystal can lead to a difference in their lattice parameters and therefore to strain at the boundary NC/microcrystal. The mono- or bi-axial strain will reduce [16] the symmetry of the distorted lattice to, correspondingly C_s or C_i, and to splitting of the $F_{2g}(\Gamma)$ on $2A'+A''$ or $A'+2A''$ and $E_g(L)$ on $A'+A''$. Subsequently the anharmonic interaction and Fermi resonance between the sum modes of the acoustical phonons from L point of the Brillouin zone with A' or A'' optical modes of the Γ point will take place, leading to the doublet structure of the observable phonon peak (in Raman spectrum the full symmetry, A' state is dominant one).

The occurrence of the Fermi resonance for NCs may be expected, because this effect was observed even in bulk Si under pressure due to a special structure of the phonon bands. It was before noted [17,18] that under pressure along ⟨111⟩, the symmetry in the point Γ is reduced from O_h to D_{3d}, and triply degenerated state F_{2g} gets split into doubly degenerated E_g and non-degenerated A_{1g}. This means the combinational mode corresponding to the point L with symmetry D_{3d} [19], which is the sum of the doubly degenerated E_g ($\Omega_{TA} \approx 114\ cm^{-1}$) and non-degenerated A_{1g} ($\Omega_{LA} \approx 378\ cm^{-1}$) vibrations, also has symmetry E_g (because $E_g \times A_{1g} = E_g$ and $\Omega_{comb} = \Omega_{LA}(\pm k_L) + \Omega_{TA}(\mp k_L) \approx 492\ cm^{-1}$). Therefore, this vibrational mode can participate in the Fermi resonance with close in frequency ($\Omega_{LO,\ TO} \approx 520\ cm^{-1}$) splitted off E_g-vibration from the Γ-point. As a result the Fermi doublet will be observed in the Raman spectrum in E_g symmetry giving rise to essential redistribution of intensities between components of doublet.

In the case of NCs, the strain can arise not only along the axis of symmetry, but in two or more directions, leading to the symmetry C_s or C_i. This general case will be considered theoretically further in this paper. It should be noted that at the full lifting of the degeneracy, side effects are possible. For example, interaction of the vibrations via fourth-order anharmonicity of the fundamental vibrations of the same symmetry, A' or A'', are created at complete splitting of the F_{2g} and E_g states, but this effect is less probable due to small magnitude of the fourth-order anharmonic constant.

It should be noted that most of the published works on electron and phonon spectra in semiconductor NCs have been focused on establishing the effect of the spatial confinement on the spectral properties of the NCs. The energy (frequency) difference of the maxima of spectral resonances (excitonic or phonon), the bandwidth and lineshape is determined first of all by the size-dependent localization of the electron or phonon wave function. Despite the fact that the frequency shifts of the resonances can be very large, they still can be well described by traditional methods of solid state theory, down to NC size as small as several nanometers. Similarly, the downward shift and asymmetrical broadening of the optical phonon peak can be described (within certain NC size range) by a rather simple model of phonon confinement [20]. At the same time, another important consequence of size reduction for phonons in NCs is the enhancement of anharmonicity due to increase of the amplitude of the vibrations of the surface atoms. The latter effect can be important for Si NCs under study here. Really, it should be kept in mind that the amplitude of the atomic vibrations (especially of surface ones) of the NCs increases noticeably under heating and can lead to reduction of the crystal symmetry. As a result, the degenerated states can split and give additional band(s) in Raman spectrum.

Due to lifting of degeneracy the new anharmonic interactions can be revealed which are known to affect position and intensities of bands. It should be noted that effects related with temperature and anharmonicity in the crystal dipole moment (optical anharmonism) were considered previously for explanation of strong temperature dependence of absorption bands in hydrogen bonded crystals [21]. The effect of optical anharmonism was studied in the temperature range of 77–300 K. At much higher temperatures the effect of high order anharmonic constants in potential energy (mechanical anharmonism) can become important. In the theoretical approach developed in this work, the effect of the above kinds of anharmonicity on the Raman spectra will be considered.

3. Short theory of Fermi resonance interactions and temperature effects

3.1. General symmetry properties of Si crystal

Silicon belongs to O_h^7 space group [19]. Unit cell of such crystal is the face-centred one and contains two identical atoms. The symmetry group at point Γ coincides with group of wave vector $\vec{k}$ of direction in this point and is O_h. The point L corresponds to a center of six-angle in the first Brillouin zone and is characterized by D_{3d} symmetry group. Ab initio calculations and experiments show [22] that the points Γ and L in Si crystal correspond to the following Raman modes: triple degenerated F_{2g} with $\omega_{TO}(\Gamma) = \omega_{LO}(\Gamma) = 520\ cm^{-1}$, double degenerated