Modeling of Brillouin Spectrum of a Quantum Dot Crystal

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ABSTRACT

We consider a novel type of nanostructures, which consists of closely spaced 3D-regimented arrays of semiconductor quantum dots. The analogy with “real” crystals in such structure is reinforced by strong carrier and phonon spectrum modification, which leads to the formation of mini-bands. Thus, we refer to this structure as quantum dot crystal (QDC). Brillouin spectroscopy is expected to provide useful information on the phonon spectrum modification in such nanostructures. In order to help with interpretation of experimental spectra, we develop a theoretical model and carry out simulation of Brillouin spectrum of a regimented array of quantum dots. The phonon spectrum of Ge$_x$Si$_{1-x}$/Si QDC is found from the numerical solution of the elasticity equation for the whole structure. It is shown that our approach allows one to include the effect of the matrix, e.g., barrier material, as well as dot regimentation, and lead to solutions different from simple Lamb-type calculations.

Keywords: quantum dot crystal, quantum dot superlattice, confined phonons, nanostructures, optical spectroscopy.

1. THEORETICAL MODEL

The light scattering spectroscopy has proven to be a powerful tool for investigation of arrays of semiconductor quantum dots, nanoparticles, as well as of nano- and microcrystalline multilayers. It is capable of providing information on modification of vibration spectra of such structures as well as on carrier confinement [1-3]. Of special interest are phonon confinement effects in quantum dots (QD) and nanocrystals. They manifest themselves via appearance of additional peaks in low-frequency range, blue shift of confined acoustic phonon peaks with the decreasing nanoparticle size, as well as red shift and asymmetric broadening of optical phonon peaks.

Two different types of the light backscattering spectroscopy with phonon participation are usually defined as Brillouin spectroscopy (for acoustic phonons) and Raman spectroscopy (for optical phonons). However, the essence of Raman and Brillouin spectra is the same. The only difference is that it is common in Raman spectroscopy to neglect the tiny change of the optical phonon energy in comparison to its value at zero wave-vector since optical phonons have flat dispersion near the center of the Brillouin zone. We include phonon dispersion in our calculations and thus mostly refer to the obtained spectra as Brillouin spectra. On the other hand, it is more common to refer to experimental results and discuss effect of the symmetry in terms of Raman spectra.

Interpretation of spectra obtained in Raman scattering experiments with quantum dot samples is plagued with uncertainties and is a subject of continuous debates. It is often difficult to determine whether the change in location and shape of Raman peaks is due to strain, alloying, interdiffusion or it is induced by spatial confinement. When quantum dots form a regimented array, the interpretation of Brillouin spectra becomes even greater challenge owing to possible appearance of additional phonon dispersion branches, e.g. standing waves inside or between quantum dots, etc. [4]. This presents a strong motivation for theoretical investigation of Brillouin and Raman spectra of quantum dot arrays.

In this paper we present our model based on numerical solution of the elasticity equation for the whole structure rather than for separate dots, which allows for accurate interpretation of Raman spectra of three-dimensional (3D) regimented arrays of quantum dots. We argue that it is essential to consider the vibration spectrum of the whole structure in order to obtain correct peak positions and separate the effect of strain or interdiffusion from phonon confinement.

Regimented or partially regimented 2D and 3D arrays of multiple quantum dots of different symmetry, have been fabricated by a variety of techniques [5]. In order to simplify the numerical solution of the elasticity equation for the heterogeneous system of QDC we restricted our analysis to orthorhombic QDC structure shown in Fig. 1. At the same time, this simple structure allows us to elucidate the effects of regimentation on the phonon dispersion and optical spectra. The feature size of QDC (3nm - 9nm) was chosen to be much smaller than the phonon mean-free path and laser wavelength ($\lambda=514$ nm) yet it is large enough for application of the elastic continuum approximation (see applicability limits discussed in Ref. [4]).

We consider the low frequency part of spectrum where we expect the most pronounced effects of
are components of photoelastic tensor. In semiconductors of cubic symmetry there are only 2 independent non-vanishing components of the photoelasticity tensor \( q_{1111} \) and \( q_{1122} \). Thus \( \varepsilon_{ij} \) perturbed by phonons has only its diagonal components

\[
\varepsilon_{xx} = \varepsilon_{0x} + q_{1111} \frac{\partial U_x}{\partial x} + q_{1122} \frac{\partial U_y}{\partial y} + q_{1122} \frac{\partial U_z}{\partial z},
\]

with similar expressions for \( \varepsilon_{yy} \) and \( \varepsilon_{zz} \) obtained by cyclic exchange of \( x, y, \) and \( z \).

Electromagnetic wave with frequency \( \omega \) and wave vector \( \mathbf{k} \) in optically isotropic medium can be characterized by \( \mathbf{D} = \varepsilon_0 \mathbf{A} \exp(i \mathbf{k} \cdot \mathbf{r}) \exp(-i \omega t) \). Here \( \varepsilon_0 \) is dielectric susceptibility of vacuum, \( \mathbf{A} \) is the light polarization vector, which is perpendicular to the direction of the wave propagation, \( \mathbf{k} = 2\pi n / \lambda \), and \( \lambda \) is the light wavelength in vacuum. The probability of the scattering process from state \( \mid \mathbf{D}_i \rangle \) to \( \mid \mathbf{D}_f \rangle \) is proportional to the square of the projection of the initial state onto the final one. Since all the eigenstates are orthogonal, the allowed processes are either from the state perturbed by phonon vibration to the unperturbed state, or vice versa. The first process corresponds to light scattering with phonon absorption leading to anti-Stokes peak shift and the second one corresponds to phonon emission, e.g. Stokes shift. Multi-phonon processes are also allowed but with much less intensity.

Here we limit consideration to one-phonon anti-Stokes processes. The intensity of Stokes peaks in experimental spectra can be found by scaling with Boltzmann factor. The probability of the scattering process from state \( \mid \mathbf{D}_i \rangle \) to \( \mid \mathbf{D}_f \rangle \) is found as \( P_{\beta} \propto | \langle \mathbf{D}_i | \mathbf{D}_f \rangle |^2 \).

Substituting expression for \( \mathbf{D} \), taking into account that \( \mid \mathbf{D}_i \rangle \) corresponds to electromagnetic wave in QDC with dielectric susceptibility (Eq. (1)) perturbed by phonons and applying quasi-periodic boundary conditions, we find the final equation

\[
P_{\beta} \propto \left| \mathbf{A}_f \right|^2 \int_{E \in C} \left[ \frac{V}{d_x, d_y, d_z} \right] \left| \mathbf{k} \bullet \mathbf{r} \right|^2 \exp(-i \mathbf{q} \cdot \mathbf{r}) \cdot \left( q_{1111} A_i^I A_i^I + q_{1122} \left( A_i^I A_j^I + A_j^I A_i^I \right) \frac{\partial U_x}{\partial x} + \left( q_{1111} A_i^I A_i^I + q_{1122} \left( A_i^I A_j^I + A_j^I A_i^I \right) \frac{\partial U_y}{\partial y} \right) + \left( q_{1111} A_i^I A_i^I + q_{1122} \left( A_i^I A_j^I + A_j^I A_i^I \right) \frac{\partial U_z}{\partial z} \right)^2 \right].
\]

Eq. (2) in effective optical medium approximation correlates with conventional Raman tensor \( \mathbf{R} \) for the whole QDC structure \( P_{\beta} \propto \left| \mathbf{A}_f \cdot \mathbf{R} \cdot \mathbf{A}_i \right|^2 \), where
\[ R_{xx} \approx \int_{E_C} \exp(-i \mathbf{q} \cdot \mathbf{r}) \left[ q_{1111} \frac{\partial u_x}{\partial x} + q_{1112} \left( \frac{\partial u_y}{\partial y} + \frac{\partial u_z}{\partial z} \right) \right] d\mathbf{r} \]  

Expressions for \( R_{xy} \) and \( R_{xz} \) can be obtained by cyclic change of \( x \), \( y \), and \( z \).

2. RESULTS AND DISCUSSION

We carry out numerical simulation for GeSi quantum dots on Si. Fig. 2 shows phonon dispersion for cubical QDC with the dot size of \( L = 3.0 \text{ nm} \) and the period of \( D = 9.0 \text{ nm} \). The relative error of calculations carried out for 30 nodes in every direction is less than 1\% for the developed finite-difference scheme. It is usually assumed that in normal-incidence back-scattering configuration the Raman spectroscopy probes the zone-center phonons since transfer momentum is very small compared with the Brillouin zone size, e.g., the wavelength of light is several orders of magnitude larger than the lattice constant. The specific of Raman spectroscopy of regimented arrays of quantum dots is that the momentum \( |\mathbf{q}| \approx 2 \| \mathbf{k} \| \) is comparable with the size of the quasi-Brillouin zone (QBZ) as indicated by arrow in Fig. 2. Thus, it is important to know the phonon dispersion accurately when analyzing Brillouin spectra of QDC. In this figure, the double degenerate transverse mode is marked by \( 2\Gamma \), while longitudinal and mixed modes are marked by as \( L \) and \( M \), respectively. Note, that each phonon branch changes the symmetry of the corresponding vibration in the regions of QBZ where it interacts with other branches.

In Fig. 3 we present calculated Raman spectrum of cubical Ge, Si, /Si QDC for different atomic fraction \( x \) of Ge in Ge, Si, , quantum dots. In this calculation we assumed that the change in atomic fraction \( x \) leads to a linear change in materials parameters and used homogeneous broadening of 0.05 cm\(^{-1}\). The lowest wave number peak seen in Fig. 3-5 corresponds to the lowest longitudinal acoustic phonon mode of the bulk material. As expected its position is almost not sensitive either to change in atomic fraction or geometry. In the back scattering geometry with the normal incidence of light parallel to [001] direction of the host cubic semiconductors, the phonon modes are Raman active if they have longitudinal component of vibrations. Indeed, transverse modes only produce shear vibrations with \( \partial u_x/\partial x = \partial u_y/\partial y = \partial u_z/\partial z = 0 \) which do not contribute to \( P_{ij} \) (see Eq. (2)). The change in Ge atomic fraction (Fig. 3) leads to two noticeable effects: the shift of Raman peaks and redistribution of their intensity, e.g., gradual damping of the signal from the third branch and increase of the signal from the upper longitudinal and mixed modes. The latter can be traced back to the symmetry breaking of the displacement.

A change in the inter-dot distance between Ge dots in Si matrix (see Fig. 4) causes nonlinear redistribution of intensities. In two limiting cases of infinitely small and infinitely large inter-dot distances QDC evolves to bulk Ge or Si, respectively. Correspondingly, only the lowest longitudinal mode is active. The upper longitudinal and mixed modes are most intensive when the symmetry breaking is highest. It is achieved when the dot size \( L \) is comparable with the inter-dot distance \( H \). The shrinking of the QBZ with increasing \( D = H + L \) results in the red shift of

![Fig. 2. Phonon dispersion of Ge/Si cubic QDC with \( L_x = L_y = L_z = 3.0 \text{ nm} \); \( D_x = D_y = D_z = 9.0 \text{ nm} \).](image)

![Fig. 3. Transformation of Raman spectrum of Ge, Si, /Si cubic QDC with \( L_x = L_y = L_z = 3.0 \text{ nm} \); \( D_x = D_y = D_z = 9.0 \text{ nm} \) with increasing of the Ge content \( x \) in the solid solution of the QD material.](image)
Fig. 5 illustrates the effect of the dot shape, i.e., the symmetry breaking, on Brillouin spectra. The presented results are for the dots with constant base ($L_x = L_y = 3.0$ nm; $D_x = D_y = 9.0$ nm) and changing height of the quantum dot along [[001]] quasi-crystallographic direction. The inter-dot distance is fixed at $H_z = L_z$. One can see significant redistribution of the peaks intensity and strong shift of some peaks, which is a combined effect of the QBZ size decrease in [[001]] quasi-crystallographic direction and strong modification of phonon dispersion with change of the symmetry. The position of each peak can be traced back to the calculated dispersion (see Fig. 2).

One should note here that the peaks in Fig. 3-5 have more complicated structure than typical doublets observed in Raman scattering from folded acoustic phonons in quantum well superlattices. The position of these peaks could not be deduced from Lamb-type models that use eigenmodes of free-standing nanocrystals.

3. CONCLUSIONS

Our proposed modeling approach allows for an accurate analysis of experimental Raman spectra of quantum dot arrays. It can be used to account for the effects of dot regimentation, matrix materials and assist in separation of the spatial confinement effects from alloying and interdiffusion.

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REFERENCES


[6]. Standard ARnoldi PACKage (ARPACK) software package is available free of charge at http://www.caam.rice.edu/software/ARPACK/