Light Scattering Spectroscopies of Semiconductor Nanocrystals (Quantum Dots)

Peter Y. Yu(1), Grant Gardner(2), Shinji Nozaki(3) and Isabelle Berbezier(4)

(1) Department of Physics, University of California, Berkeley, CA and Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720
(2) Physics Department, University of Washington, Seattle, WA
(3) Department of Electronic Engineering, University of Electro-Communications, Tokyo, 182-8585 Japan
(4) L2MP, Ecole Polytechnique Universitaire de Marseille, 13451 Marseille, France

Corresponding author email address: PYYU@LBL.GOV

Abstract. We review the study of nanocrystals or quantum dots using inelastic light scattering spectroscopies. In particular recent calculations of the phonon density of states and low frequency Raman spectra in Ge nanocrystals are presented for comparison with experimental results.

1. Introduction & Background

Nanocrystals (NC) or Quantum Dots (QD) have recently received much interest because of their potential applications in devices ranging from lasers to single electron transistors[1]. So far most of the NC samples prepared by diverse techniques are inhomogeneous in their size distribution. Since most of the NC properties are determined by their size and shape [2] it is important to develop techniques capable of determine the average size and distribution of NC in a given sample. Optical techniques, as compared to direct imaging techniques like high resolution transmission electron microscopy, have the advantages that they are non-destructive and require minimum sample preparation. In this paper we will review the use of light scattering techniques for determining size distributions in NC samples. In particular, we show that as a result of recent theoretical understanding of the low frequency vibrational modes of spherical NC, light scattering spectroscopy from these modes provides a simple and yet powerful technique for determining the size of NC. We will demonstrate this by comparing the experimental and theoretical results obtained on Ge NC prepared by a new technique of co-evaporating Si and Ge following by oxidation of Si into SiO$_2$[3,4].

So far spectroscopic techniques applied to study NC includes absorption, photoreflectance (PR), photoluminescence (PL), PL excitation (PLE), Raman scattering (RS) and resonant Raman scattering (RRS) [5]. While theoretically one expects that optical
transitions in NC should produce sharp peaks due to quantum confinement in all three directions, in reality these absorption peaks are often broadened by inhomogeneous size distributions to form smooth structures. Various optical “tricks”, such as spectral hole burning [6] and selectively excited PL[7], have successfully been applied to extract sharp features out of the broadened optical spectra. However, most of these techniques can be applied only to specific types of samples. For example, selectively excited PL can be applied only to samples which are strong emitters. Spectral hole burning cannot be applied easily to large band gap insulators nor to metallic NC.

In principle, there is one technique, namely, inelastic light scattering spectroscopy which can be applied to any type of sample. In a typical medium, whether a solid, liquid, or gas, light can be scattering by fluctuations in the medium[8]. Fluctuation produced by molecular vibrations give rise to Raman scattering from optical phonons. There have been many reports of using the confinement effect on optical phonon frequencies to determine the NC size [9]. However, optical phonon frequencies can depend not only on confinement but also on strain. In addition, this method is more sensitive for small NC. Finally, solids containing only one atom per unit cell (such as many metals) do not have optical phonons. One kind of fluctuation which always exists in any medium is that of density. This can be caused by longitudinal oscillations associated with pressure (or sound) waves. In a solid medium transverse oscillations associated with shear waves can also scatter light. This kind of inelastic scattering is commonly known as Brillouin scattering[8]. For long wavelengths λ (or small wave vectors q) the dispersion relation between the (angular) frequency ω and λ is linear:

\[ \omega = v(2\pi/\lambda) = vq \]  

where \( v \) is the velocity of the wave. 

This linear relation breaks down when \( \lambda \) is comparable to the inter-atomic distances. In infinite media with translational symmetry the wave vector \( q \) involved in the scattering is determined by the wave vectors of the incident and scattered light (\( k_i \) and \( k_s \)) via the conservation law [8]:

\[ q = k_i - k_s \]  

(2)

In NC, however, the λ of allowed mechanical waves are determined by the NC size just as the length of a violin string determines the wavelengths of its longitudinal standing waves. Specifically, in a spherical NC of diameter D the largest \( \lambda \) is given by 2D or the smallest \( \lambda \) possible scales as (1/D). This relation between \( \omega \) and D is valid for some of the higher frequency modes in NC except for the optical phonons. Thus it is possible, in principle, to determine the size of the NC from Brillouin scattering.

So far there has been a number of reports of the low frequency Brillouin scattering from semiconductor NC[10]. The linear relation between \( \omega \) and (1/D) was observed. However, the constant of proportionality between \( \omega \) and (1/D) is no longer given simply by the phonon velocities as in Eq. (1). Instead this constant is a function of the bulk transverse and longitudinal acoustic (TA and LA) phonon velocities (\( v_T \) and \( v_L \)). The dependences on \( v_T \) and \( v_L \) is sensitive to the mechanical model used to calculate the vibrational properties of the NC. In the literature an elastic continuum model for a sphere proposed by Lamb [11] is often used to interpret the experimental data and to calculate the constants of proportionality. For example, Tanaka et al. have used this theory to explain the low frequency Raman modes they observed in CdS NC [12]. However, they found ambiguity in identifying some of the Raman modes since these modes appear both in polarized and depolarized spectra. According to group theory only spheroidal modes whose displacement vectors have vanishing curls are
Raman-active. Often the lowest frequency peak in the scattered spectra is identified in terms of torsional modes whose displacement vectors have vanishing divergence and are predicted to be forbidden by selection rules[13]. Thus the experimental observation of a break-down in the selection rule has raised questions about the exact identification of the observed Lamb modes and hence the constant of proportionality between \( \omega_{sp} \) and \( \omega_t \) and \( (1/D) \). A further challenge lies in the validity of the Lamb model which is expected to breakdown when D becomes comparable to the lattice constant. Since the exact value of D when this breakdown occurs is usually not known it is not clear that the Lamb model applies to NC with D~ 1-5 nm, a range of size for many NC of interest.

To address the above difficulties of determining NC from low frequency phonon modes, lattice dynamical models have recently been developed to study both the frequencies and the Raman intensities of phonon modes in Ge NC [14]. The model is based on a two-parameter Keating model with additional simplification based on group theoretical analysis. With these simplifications the phonon density-of-states in Ge NC with the total number of atoms \( N \) varying between ~100 to ~10^4[14]. Using a simple polarizability model, Raman intensity and selection rules for the low frequency phonon modes have also been obtained[15]. The theoretical results show that in case of Ge NC the Lamb model breaks down for D<4 nm. It also found that the Raman selection rules of the Lamb modes predicted by group theory are valid. The lowest frequency mode commonly identified as a torsional Lamb mode should be attributed to the \( n=0 \) and \( l=2 \) spheroidal mode when D is large enough for the Lamb model to be valid. The next higher frequency mode, usually observed in the parallel scattering geometry, should be the \( n=1 \) and \( l=0 \) spheroidal mode. Within the lattice dynamical model the lowest frequency mode should belong to the \( E \) irreducible representation of the \( T_d \) group. Almost degenerate with the \( E \) mode is the \( T_2 \) mode while the \( A_1 \) mode is the higher frequency one usually attributed to the spheroidal Lamb mode.

As an experimental test of this new microscopic model in determining Ge NC size we have applied it to understand the results obtained from Ge NC embedded in SiO\(_2\) grew by a new fabrication technique.

2. Ge Nanocrystal Sample Preparation
The Ge NCs in our study were formed by growing a 1.8 nm-thick strained Ge layer on the 100 nm-thick Si buffer layer on a Si substrate at 550 °C by the molecular beam epitaxy (MBE). Prior to the growth of the Ge layer, a monolayer of Sb surfactant was deposited on the Si buffer layer to promote nucleation of small Ge islands via Stranski-Krastanov growth. After the Ge growth only circular domes of Ge were observed with a diameter of ~30 nm and a height of 1 nm as determined by Atomic Force Microscope [3]. The structure was then capped by a 10 nm-thick Si layer. To form QD the as-grown samples were dry oxidized at 900 °C for 2 hours so that Si was oxidized to SiO\(_2\) as shown by transmission electron micrographs. The subsequent Raman spectra demonstrated that the annealing also promoted mixing of Si and Ge rather than formation of well-defined QD. As an alternate approach the sample was annealed at a lower temperature such as 400 °C for 4 hours while under illumination by uv light using a lamp with a peak wavelength between 380 and 390 nm. The light intensity on the sample was 500 mW/cm\(^2\). The photo-oxidation of the Ge NCs were observed under UV irradiation [4]. These samples will be labeled as “Photo”.
3. Experimental Light Scattering Results
The light scattering spectra were measured at room temperature from the Ge samples by exciting the sample with the various lines of an Ar ion laser and analyzing the scattered radiation with a Spex double monochromator. As an example, Figure 1 shows the optical phonon Raman spectrum of the as-grown Ge island on Si(100) substrate. For comparison the Raman spectrum of the Si substrate is also shown. Since there is significant overlap between the Raman spectra of Ge and Si, the spectrum of the Ge layer alone is obtained by subtracting from the Ge/Si spectrum the Si Raman spectrum[8]. The resultant spectrum is dominated by 2 peaks around 300 and 410 cm\(^{-1}\). They are identified usually in the literature as due, respectively, to vibration of the Ge-Ge and Ge-Si bonds[16]. This spectrum resembles the spectrum of bulk SiGe alloy containing 22% of Si reported by Renucci et al. [16] and suggests a strong mixing of Si and Ge atoms upon thermal annealing.

After the as-grown samples were annealed and oxidized under uv illumination, they were found to be inhomogeneous. The sample appears to be cloudy in certain regions and the Ge Raman signal was stronger in some region than in others. There is also enhanced scattering of the laser plasma lines as a result of the inhomogeneity. It becomes necessary to remove some of the stronger plasma lines so that they do not mask the broader Ge peaks. The resultant Raman spectrum is shown in Fig. 2. In this spectrum the Ge-Ge and Si-Ge peaks are visible again although the quality of the signal is poorer. The interesting new result in these "photo-oxidized" samples is that whenever we see evidence of Ge in the optical phonon region we also see peak in the low frequency region which have been attributed to Lamb modes[17]. An example of such spectra is shown in Figure 3. We note that the frequency of the peak in the crossed-polarization (V-H) spectrum is lower than in the polarized (V-V) spectrum. An indication of the size inhomogeneity of the sample is that the frequencies of these two peaks can vary from one region of the sample to another by as much as 18%. However, the ratio of the frequencies of these two peaks (\(\omega_{VV}/\omega_{VH}\)) remains constant and equal to \(~1.8\) indicating that they come from the same nanocrystals.

4. Discussions
To comparing our observed low frequency modes with those calculated by Cheng et al. [15] we assumed that the lowest frequency E and T\(_2\) modes are degenerate and contribute mainly to the VH polarized spectrum. The theoretically calculated ratio \(\omega_{A1}/\omega_{E+T2}\) is equal to 1.7 with no adjustable parameter. From the frequency of the polarized VV mode (which we attribute to the A\(_1\) mode in the lattice dynamical calculation) we determine the diameter D of the Ge NC in our sample to be \(~12\) nm. We note that Ovsyuk et al.[17] have also reported the low frequency Raman spectra of Ge NC with D\(~13\) nm. They observed a frequency of \(~10\) cm\(^{-1}\) and \(~7\) cm\(^{-1}\) for the polarized and depolarized spectra respectively. Thus their Raman frequencies are in good agreement with our values for NC of comparable diameters. However, we would now attribute both Raman peaks to spheroidal Lamb modes. Based on the microscopic theory we can now estimate the size distribution of the NC in our sample from the width of the Raman peaks. After subtracting out the spectrometer slit width we estimated a NC size distribution of about 9% within our laser focal spot of \(~10\) \(\mu\)m. As noted earlier the size distribution over the whole sample area of several mm is twice as large.

For Ge NC with D\(>10\) nm the optical phonon confinement model would not be sensitive enough to determine the size and distribution of NC.
5. Conclusions
In summary, we have shown that light scattering spectroscopies are powerful and yet nondestructive techniques for estimating the size and distribution of nanocrystals. In case of small Ge NC Raman scattering from confined optical phonons (with correction for strain) can be used. For larger NC Brillouin scattering from low frequency Lamb modes is a more sensitive technique.

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FIGURES AND CAPTIONS

Figure 1  A typical Raman spectrum of the as grown sample in the high frequency range between 200 and 500 cm⁻¹.

Figure 2  Raman spectrum of Ge/Si layer after oxidation and annealing under uv illumination.

Figure 3  Polarized low frequency Raman spectra of Ge/Si layers after oxidation and annealing under uv illumination.