Raman Spectroscopy of InAs/GaAs Quantum Dots Patterned by Nano-Indentation

by

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A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science Department of Physics College of Arts and Sciences University of South Florida

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Dedication

This work is dedicated to Amalia, Ariana and Alexandra Fragoso.
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I would like to thank Dr. Martin Munoz, Dr. Curtis Taylor, Dr. Durig Lewis and Laura Akesson. Without their help this work would not have been possible. I would also like to thank my parents, my family and my wonderful friends.
# Table of Contents

List of Figures .................................................................................................................................................. i

List of Tables ...................................................................................................................................................... ii

Abstract............................................................................................................................................................ iii

Chapter 1. Fundamentals of Raman Spectroscopy ...................................................................................... 1

1.1 Introduction................................................................................................................................................ 1

1.2 Classical Treatment of Raman Shift ....................................................................................................... 2

1.3 The Raman Tensor and Selection Rules .................................................................................................. 4

1.4 Experimental Setup.................................................................................................................................. 8

Chapter 2. Raman Spectroscopy of Nano-Indented Quantum Dots ......................................................... 13

2.1 Introduction................................................................................................................................................ 13

2.2 Sample Description.................................................................................................................................. 14

2.3 AFM Results............................................................................................................................................. 15

2.4 Raman Results......................................................................................................................................... 16

2.5 Analysis: Identification of Raman Modes .............................................................................................. 18

2.6 Analysis: Strain Calculation....................................................................................................................... 22

Chapter 3. Conclusions ..................................................................................................................................... 26

References.......................................................................................................................................................... 27

Appendices........................................................................................................................................................ 28

Appendix A Mathematica Calculation of Quantum Dot Interface Modes ........................................ 29
List of Figures

Figure 1: Comparison of Raman and PL signal intensities.................................1

Figure 2: Illustration of x, y and z directions within sample geometry ...............7

Figure 3: Internal components of HR 800 ............................................................9

Figure 4: Horiba Jobin Yvon HR 800 micro-Raman System ..........................10

Figure 5: Path of light in Raman System .........................................................11

Figure 6: Microscope Objective and Spectrograph Grating ............................12

Figure 7: InAs coverage versus 3D Island Density .........................................14

Figure 8: Schematic of InAs dot on GaAs buffer layer ..................................15

Figure 9: AFM Images of InAs QDs grown by nano-indentation (increasing tip load) .........................................................................................................................15

Figure 10: Scattering Intensity versus wavenumber of 200µN nano-indentated samples .......................................................................................................................17

Figure 11: Scattering Intensity versus wavenumber of 500nm nano-indentated samples ......................................................................................................................17

Figure 12: QD orientation diagram and hydrostatic and biaxial strain distribution along the center of a pyramidal QD (Z (001) direction) .................................22

Figure 13: Wavenumber vs. QD height .............................................................25
List of Tables

Table 1: Selection Rules for zincblende materials\textsuperscript{3} ............................................................8

Table 2: Samples with fixed load......................................................................................16

Table 3: Samples with fixed indentation spacing. ............................................................16
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ABSTRACT

Patterns of InAs/GaAs quantum dots (QDs) grown by the combination of nanoindentation technique and molecular beam epitaxy were studied. The resulting QDs tend to preferentially nucleate on indented areas rather than other regions. We studied the strain on the indentations, regions surrounding the indents, and non-indented areas. The QD LO mode for the patterned areas shifts by 7 cm$^{-1}$ when compared to the non-patterned area. The biaxial strain in the indented areas producing this shift is four times larger than that in non-indented areas, explaining the QD preferential formation within these areas. This larger strain suggests that QDs on the indentations can be formed by depositing a smaller InAs amount than that required to form QDs on non-indented areas, thus obtaining QDs only on the pattern.
1.1 Introduction

When light is incident on a material several processes can occur; light can be reflected, transmitted, absorbed or scattered. Raman Scattering is a second order process consisting of the inelastic scattering of incident photons by phonons (lattice vibrations). As illustrated by Figure 1\textsuperscript{1}, Raman Scattering (RS) is extremely weak when compared to other optical processes such as Photoluminescence. However, with the development of lasers and ultra-sensitive detectors, Raman Spectroscopy (RS) has become an extremely useful tool for investigating properties of semiconductors such as phonon modes, doping levels, crystalline quality, impurity concentration and strain.

![Raman and PL signal intensities](image)

Fig. 1 Comparison of Raman and PL signal intensities of Cd_{0.72}Mn_{0.28} Te film on a GaAs substrate\textsuperscript{1}
1.2 Classical Treatment of Raman Shift

The interactions of the incident photon with the phonon modes within a material lead to a shift in photon frequency, referred to as the Raman shift. Some outgoing photons will be shifted to higher energy (a phonon is absorbed) or lower energy (a phonon is emitted). These shifts are called anti-Stokes (higher energy) and Stokes (lower energy), respectively. The quantum mechanical treatment of RS is very complex\(^1\) and will not be provided here but can be found in Ref. 2. In this thesis RS will be treated in a classical perspective for the reader to achieve a basic understanding of the process.

The nonlinear Raman interaction depends on the polarizability of the material on which light is incident, we note that the dielectric function will vary slightly with lattice spacing and the electric susceptibility changes due to the excitation of the material\(^1\).

We begin our discussion by introducing a monochromatic electromagnetic plane wave of the form,

\[
\mathbf{F}(r,t) = \mathbf{F}(\mathbf{k},\omega) \cos(\mathbf{k} \cdot \mathbf{r} - \omega t) \quad (1)
\]

into some medium. This electric field will induce a polarization

\[
\mathbf{P}(\mathbf{r},t) = \mathbf{P}(\mathbf{k},\omega) \cos(\mathbf{k} \cdot \mathbf{r} - \omega t) . \quad (2)
\]

The polarization will have the amplitude:

\[
\mathbf{P}(\mathbf{k},\omega) = \chi(\mathbf{k},\omega) \mathbf{F}(\mathbf{k},\omega), \quad (3)
\]

where \(\chi\) is the electric susceptibility. The frequency and wavevector of the polarization is the same as those of the incident radiation. The electric susceptibility will fluctuate due
The normal modes of these atomic vibrations are called phonons.

We can express the displacement of atoms associated with a phonon as plane waves:

$$Q(r,t) = Q(q, \omega_{ph}) \cos(q \cdot r - \omega_{ph}t)$$  \hspace{1cm} (4)

where $\omega_{ph}$ and $q$ are the phonon frequency and wavevector, respectively.

The electron frequencies which contribute to the electric susceptibility are much higher than $\omega_{ph}$ therefore we can take $\chi$ to be a function of $Q$ and expand it as a Taylor series in $Q(r,t)$:

$$\chi(k_i, \omega_i, Q) = \chi_0(k_i, \omega_i) + \left(\frac{\partial \chi}{\partial Q}\right)_0 Q(r,t) + ...$$  \hspace{1cm} (5)

The first term of equation (5) represents the electric susceptibility with no atomic fluctuations and the second term represents the fluctuations induced by the phonon wave $Q$. Using this expression for the electric susceptibility we can rewrite the polarization as:

$$P(r,t,Q) = P_0(r,t) + P_{ind}(r,t,Q)$$  \hspace{1cm} (6)

where,

$$P_0(r,t) = \chi_0(k_i, \omega_i)F_i(k_i, \omega_i) \cos(k_i \cdot r - \omega_it)$$  \hspace{1cm} (7)

and,

$$P_{ind}(r,t,Q) = \left(\frac{\partial \chi}{\partial Q}\right)_0 Q(q, \omega_{ph}) \cos(q \cdot r - \omega_{ph}t)F_i(k_i, \omega_i) \cos(k_i \cdot r - \omega_it).$$  \hspace{1cm} (8)

Equation (7) is a polarization vibrating in phase with the incident electromagnetic radiation and Eq. (8) is a polarization induced by the phonon.

We determine the frequency and wavevector of the polarization induced by the
phonon by rewriting Eq. (8) as

$$P_{\omega}(r,t,Q)=\frac{1}{2}\left(\frac{\partial^2}{\partial Q^2}\right) Q(q,_{\alpha\beta}\)\{r(k,_{\alpha\beta}\} \times \{\cos(k, + q) \cdot r - [\alpha\beta + \alpha\beta]\} + \cos(k, - q) \cdot r - [\alpha\beta - \alpha\beta]\} \}$$  \hspace{1cm} (9)

From Eq. 9 we can see that this polarization will give origin to electromagnetic waves of frequency $\omega_i \pm \omega_{ph}$,

$$\nabla \times \nabla \times + \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \right] E(r,t) = -\mu_0 \frac{\partial^2}{\partial t^2} \cdot P(r,t). \hspace{1cm} (10)$$

This form of the phonon-induced polarization reveals two sinusoidal waves, the Stokes and Anti-Stokes shifted waves discussed previously. The Stokes and Anti-Stokes shifted waves have the wavevectors and frequencies

$$k_S = k_i - q, \quad \omega_S = \omega_i - \omega_{ph} \hspace{1cm} (11)$$

and

$$k_{AS} = k_i + q, \quad \omega_{AS} = \omega_i + \omega_{ph}, \hspace{1cm} (12)$$

respectively.

1.3 The Raman Tensor and Selection Rules

Now that we understand the origin of the Raman shift we will use this information to determine the intensity of the scattered radiation. We will also discuss the importance of scattering geometries and the determination of Raman-active phonons through the Raman selection rules. The intensity of the scattered radiation can be expressed as:

$$I_s \propto \omega_p^4 L V |\mathbf{e}_s \cdot \mathbf{n} \cdot \mathbf{e}_s|^2 \times \begin{cases} N_p & \text{Anti - Stokes} \\ N_p + 1 & \text{Stokes} \end{cases} \hspace{1cm} (13)$$
where \( \omega_s \) is the scattered frequency, \( L \) is the scattering length, \( V \) is the scattering volume \( L \) times the excitation beam area), \( N_p \) is the phonon density which is expressed as
\[
N_p = \frac{1}{\exp\left(\frac{\hbar \omega_{ph}}{k_B T}\right) - 1}
\]
and most importantly we have \( \Re \), the Raman tensor
\[
\Re = \left( \frac{\partial \chi}{\partial Q} \right)_0 \hat{Q}(\omega_0).
\]
The Raman tensor is derived from the polarization induced by the phonon, Eq. (8). \( \Re \) carries geometric information and will vary for different materials depending on their symmetry and magnetic properties. The Raman tensor is symmetric only when the frequency difference between the incident and scattered radiation is ignored. In practice this symmetry is assumed because the frequency of the laser is much larger than that of the phonon,
\[
\omega_s \text{ or } \omega_A = \omega_i \pm \omega_{ph} \approx \omega_i, \quad (\omega_{ph} \ll \omega_i)
\]
Other non-symmetric components can appear in the tensor when a magnetic field is present. Symmetry requirements lead to the non-existence of scattered radiation for certain scattering geometries, in other words for a given geometry some phonons are allowed and some phonons are forbidden.

To better acquaint ourselves with this topic, we will discuss the Raman selection rules for zincblende materials, such as GaAs and InAs which are the base materials of our structures. For zinc-blende materials, vibrations polarized in the \( x = [100], y = [010] \) and
$z = [001]$ directions have the following Raman tensors\(^3\)

\[
\mathcal{R}_x = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & d \\ 0 & d & 0 \end{pmatrix}, \quad \mathcal{R}_y = \begin{pmatrix} 0 & 0 & d \\ 0 & 0 & 0 \\ d & 0 & 0 \end{pmatrix} \quad \text{and} \quad \mathcal{R}_z = \begin{pmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}
\] (17)

where $d$ is the one linearly independent component.

Now that we have the Raman tensors in Eq. (17) we can determine the selection rules for RS in GaAs for different scattering geometries. Backscattering geometry is the geometry in which the directions of the incident and scattered photons are antiparallel to each other. Since this geometry is the one used in our experiments we will use it in our example. Let’s say we want to determine if the LO phonon is allowed for backscattering geometry on the (100) surface of GaAs. We begin with the Raman tensor

\[
\mathcal{R}_x = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & d \\ 0 & d & 0 \end{pmatrix}.
\] (18)

We use this tensor because the LO phonon is defined as the vibration in the x-direction.

The selection rules will be illustrated in the backscattering geometry over a (100) surface. Figure 2 illustrates the x, y and z directions with respect to the sample geometry.
Next we determine where the mode is allowed by imposing the incident and scattering polarizations:

\[
\Re_s e_y = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & d \\ 0 & d & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ d \end{pmatrix}
\]

and we have

\[
e_y \Re_s e_y = 0 \quad \text{and} \quad e_z \Re_s e_y = d_{LO},
\]

\[
\Re_s e_z = \begin{pmatrix} 0 \\ d \\ 0 \end{pmatrix} \Rightarrow e_y \Re_s e_z = d_{LO} \quad \text{and} \quad e_z \Re_s e_z = 0
\]

which shows that the LO phonon is allowed in this geometry\(^4\). A similar procedure can be followed for other scattering directions. Table 1 gives selection rules for other backscattering geometries on the (100) surface of zinc-blende materials. In this table, we are using Porto’s notation given by:
\[ \mathbf{k}_r (\mathbf{e}_i, \mathbf{e}_s) \mathbf{k}_s \]  \hspace{2cm} (21)

where \( \mathbf{k}_i \) and \( \mathbf{k}_s \) are the directions of the incident and scattered photons, respectively, and \( \mathbf{e}_i \) and \( \mathbf{e}_s \) are the polarizations of the incident and scattered photons, respectively. In Table 1 \( y' \) and \( z' \) denote the [011] and [0\overline{1}1] directions, respectively.

<table>
<thead>
<tr>
<th>Scattering Geometry</th>
<th>Selection Rule for (100) surface</th>
<th>TO phonon</th>
<th>LO phonon</th>
</tr>
</thead>
<tbody>
<tr>
<td>( x(y,y) \bar{x} ; x(z,z) \bar{x} )</td>
<td>0</td>
<td>0</td>
<td>(</td>
</tr>
<tr>
<td>( x(y,z) \bar{x} ; x(z,y) \bar{x} )</td>
<td>0</td>
<td>(</td>
<td>d_{LO}</td>
</tr>
<tr>
<td>( x(y',z') \bar{x} ; x(z',y') \bar{x} )</td>
<td>0</td>
<td>0</td>
<td>(</td>
</tr>
<tr>
<td>( x(y',y') \bar{x} ; x(z',z') \bar{x} )</td>
<td>0</td>
<td>0</td>
<td>(</td>
</tr>
<tr>
<td>( x'(x,x) \bar{y}' )</td>
<td>0</td>
<td>0</td>
<td>(</td>
</tr>
<tr>
<td>( x'(z',x) \bar{y}' )</td>
<td>0</td>
<td>(</td>
<td>d_{TO}</td>
</tr>
<tr>
<td>( x'(z',z') \bar{y}' )</td>
<td>(</td>
<td>d_{TO}</td>
<td>^2 )</td>
</tr>
</tbody>
</table>

Table 1 Selection Rules for zincblende materials on (100) surfaces.

1.4 Experimental Setup

A general micro-Raman system setup illustrating the paths of the excitation laser and scattered radiation is shown in Figure 3. The incoming laser radiation is reflected by the notch filter and then focused by the microscope objective on the sample. The reflected laser and scattered light are collected by the objective. The notch filter only allows the transmission of the scattered light and avoids the laser transmission to the spectrometer.
The experiments in this thesis were performed using a Horiba Jobin Yvon HR 800 micro-Raman System where the 800 refers to the 800mm focal length of the spectrograph, an illustration of the equipment is provided in Figure 4.
The Raman system includes an internal HeNe 20mW laser with a wavelength of 632.8 nm and an external HeCd 50mW laser with a wavelength of 325nm. Scattered radiation is detected by a charge coupled device (CCD) detector cooled to 77K by liquid nitrogen cooling. The computer on the setup uses LabSpec software.

As shown in Figure 5, the exciting laser radiation travels through a laser filter to remove plasma lines, afterward it passes through a pinhole mirrors and notch filter and is focused on the sample by the microscope objective. The HR800 system includes six different neutral density filters to reduce the laser intensity according to

$$I = I_0 \times 10^{-D}$$  \hspace{1cm} (22)
where $D$ can range from zero to four depending on the filter density. These neutral density filters are often used to reduce photoluminescence that may appear in a scan.

Fig. 5 Path of light in Raman System (white line represents light)\textsuperscript{4}

Since we have a backscattering setup, the Raman Scattered light is transmitted back through the microscope objective and through the notch filter where it travels to the monochromator. This notch filter rejects the laser light and allows only the scattered light to arrive at the spectrograph. The spectrograph scanning range is limited by the grating chosen. The HR800 is equipped with two gratings, 600g/mm and 2400g/mm. The 600g/mm has a scanning range of 0-2600nm and the 2400g/mm has a scanning range of 0-650nm. The spectrometer scans over a selected range and the CCD detects the intensity of the scattered light. The CCD detector was calibrated using the Raman shift of a standard silicon samples as a reference.
The microscope consists of four different objectives, one in which UV light may pass and three objectives of 10X, 50X and 100X magnification to visible light, Figure 6 is a picture of the system’s microscope and spectrograph. Along with an adjustable confocal hole (0-1000nm), we are able to control the size of the laser spot on the sample. The size of the confocal hole will influence spectral and spatial resolution.

Fig. 6 Microscope Objective and Spectrograph Gratings
2.1 Introduction

Quantum Dots (QDs) are semiconductor nanostructures of particular interest due to their confinement in three dimensions and sharp density of states. Possible applications of QDs include qubits for quantum computing, optical modulators, photonic crystals to control and manipulate the flow of light, and lasers with ultra-low threshold current. The pathway towards QD devices depends on the ability to control their size and morphology.

Strain is the driving force behind the formation of QDs. In Molecular Beam Epitaxy (MBE) QDs are grown by depositing a semiconductor with a lattice constant larger than that of the substrate, for instance InAs on GaAs or CdSe on ZnSe. There is a critical amount of the larger lattice constant material necessary to create QD structures, as shown for InAs in Figure 7. Below this critical amount only a thin, strained layer of InAs is formed. The formation of QDs by MBE has become a standard procedure however the structures that form are disorganized and vary in size and position on the surface. If the size and position of QDs can be more controlled, applications of QDs which demand more organized structures, such as qubits and photonic crystals, can be achieved with higher accuracy and confidence.
Patterning techniques are an excellent development towards preferential QD growth. Nano-indentation is a technique used to create a predefined indentation pattern on which QDs are formed preferentially. Nano-indentation can lead to a decrease in the amount of InAs necessary to create QDs, resulting in the organized formation of QDs. In this thesis we have used Raman Spectroscopy to study the strain in the nano-indentated QD structures.

2.2 Sample Description

Samples were provided by Dr. Curtis Taylor, Euclydes Marega and Ajay Malshe of the Mechanical Engineering Department at Virginia Commonwealth University, the Physics Department of the University of Arkansas and the Mechanical Engineering Department of the University of Arkansas, respectively. Samples were created by first removing the oxide layer of the GaAs substrate at 580°C under an As flux inside of a MBE chamber. A GaAs buffer layer of approximately 0.1µm is then deposited.
The sample is removed from the chamber and a diamond tip is pressed into the buffer layer to create the nano-indentated pattern. Later, the sample is reintroduced into the chamber and once again the oxide layer is removed from the sample and a GaAs buffer layer of 28nm is created. Finally, two monolayers of InAs are deposited on the sample.

![Fig. 8 Schematic of InAs dot on GaAs buffer layer](image8.png)

2.2 AFM Results

It was observed by Atomic Force Microscopy (AFM) that the QDs have a tendency to form in the indented areas. Figure 9 shows AFM images of InAs QDs of various pattern sizes and tip loads.

![Fig. 9 AFM image of InAs QDs grown by nano-indentation (increasing tip load)](image9.png)
2.4 Raman Results

Raman measurements were taken with a HR 800 micro-Raman system using a spot size of 2x2µm² and a 632.8 nm HeNe laser at room temperature. The details of this system were provided in Section 1.4. Data was taken on different indentation patterns which varied in load and indent spacing. The RS measurements were done on two sets of patterned samples, one with fixed indentation spacing (500nm) and the other with fixed load (200µN). The details of these sample sets, which correspond with the Raman data in Figures 10 and 11, are presented in Tables 2 and 3.

<table>
<thead>
<tr>
<th>Load</th>
<th>Separation</th>
</tr>
</thead>
<tbody>
<tr>
<td>200µN</td>
<td>250nm</td>
</tr>
<tr>
<td>200µN</td>
<td>500nm</td>
</tr>
<tr>
<td>200µN</td>
<td>1µm</td>
</tr>
</tbody>
</table>

Table 2: Samples with fixed load.

<table>
<thead>
<tr>
<th>Load</th>
<th>Separation</th>
</tr>
</thead>
<tbody>
<tr>
<td>400µN</td>
<td>500nm</td>
</tr>
<tr>
<td>200µN</td>
<td>500nm</td>
</tr>
<tr>
<td>100µN</td>
<td>500nm</td>
</tr>
</tbody>
</table>

Table 3: Samples with fixed indentation separation.

For comparison purposes, measurements were also taken on the non-patterned portion of the sample. The non-patterned area includes QD structures that are not organized and are not influenced by the nano-indents. AFM images of Figure 9 show examples of the unorganized QD structures formed on the outer perimeter of the nano-indent regions. Raman peaks were observed from 200-320 cm⁻¹. Figure 10 shows Raman data of the 200µN load with variable pattern spacing and Figure 11 shows data of 500nm spacing with variable tip load.
Fig. 10 Scattering Intensity versus wavenumber of 200µN nano-indentated samples.

Fig. 11 Scattering Intensity versus wavenumber of 500nm nano-indentated samples.
2.5 Analysis: Identification of Raman Modes

From the Raman data in Fig. 10 and 11 one observes three distinct peaks. The most easily identifiable peak is the bulk GaAs LO mode at 295 cm\(^{-1}\). In order to determine the origin of the other peaks we performed calculations to determine the presence interface modes and compare our data to reported values for capped InAs/GaAs QDs.

Interface modes were determined by following the method of Knipp and Reinecke\(^{10}\) in which a dielectric continuum approach is used. We begin by defining an interface mode as the propagation of electromagnetic radiation at the interface between two dielectric media\(^{11}\).

From Maxwell’s equation
\[
\nabla \cdot \mathbf{D} = \nabla \cdot [\varepsilon_i(\omega)\mathbf{E}] = \rho
\]
and with the assumption that there is no net charge within either material, we have in both the InAs and GaAs materials
\[
\varepsilon_i(\omega)\nabla \cdot \mathbf{E} = 0.
\]
In order to fulfill this condition we have two possibilities
\[
\nabla \cdot \mathbf{E} = 0 \text{ or } \nabla^2 \phi = 0
\]
and
\[
\varepsilon_i(\omega) = 0.
\] The first possibility corresponds to the case of transverse (TO) modes and the second to longitudinal (LO) modes.
In the simplest case of two slab layers the condition to have an IF mode of frequency \( \omega_{IF} \) is\(^{11} \)

\[
\varepsilon_1(\omega_{IF}) = -\varepsilon_2(\omega_{IF}). \tag{27}
\]

The general expression of the dielectric function of a media in terms of non-damped LO and TO modes is given by\(^3 \)

\[
\varepsilon_i(\omega) = \varepsilon_{\infty,i} \left( \frac{\omega_{LO,i}^2 - \omega^2}{\omega_{TO,i}^2 - \omega^2} \right), \quad i = 1,2. \tag{28}
\]

where the subscript \( i \) is 1 for the dot and 2 for the media in which the dot is embedded.

By substituting (28) into (27) and solving for \( \omega \), the frequencies of the interface modes are determined.

To determine the IF modes we will derive the electric field from a scalar potential \( \phi \) satisfying Laplace’s equation \( \nabla^2 \phi = 0 \). The scalar potential is determined by imposing traditional electrostatic boundary conditions at the interface of the two media. The tangential components of the electric field \( E = -\nabla \phi \) and the normal components of the displacement field \( D \) must be continuous.

There are few shapes for which the IF modes can be calculated analytically. These shapes are slab layers, the sphere, the spheroid and the ellipsoid. We will illustrate the general procedure for the case of a sphere of radius \( R \), we have that the electrostatic potential in spherical coordinates is

\[
\Phi(r, \theta, \phi) = e^{im\phi} P_l^m(\cos \theta) \times \begin{cases} \left( \frac{r}{R} \right)^l, & r \leq R \\ \left( \frac{R}{r} \right)^{l+1}, & r \geq R \end{cases} \tag{29}
\]

where \( P_l^m \) are Legendre polynomials of the first kind and the integers \( l \) (\( \geq 0 \)) and
$m (| m | \leq l)$ are interface mode quantum numbers$^6$. From the continuity condition of
the electric displacement across the boundary (Eqs. 26 and 27), it follows that the
eigenfrequency condition

$$\frac{\varepsilon_1(\omega_{\text{m}})}{\varepsilon_2(\omega_{\text{m}})} = -1 - \frac{1}{l}.$$  \hspace{1cm} (30)

Substituting Eq. 28 into Eq. 30 will make it possible to find the IF mode frequencies
allowed for spherical QDs. Equation 30 was solved with Mathematica for several values
of $l$ and $m$ but these values did not closely correspond to the observed IF modes. This
result is reasonable since the QDs look more like ellipsoids than spheres as evidenced by
the AFM images in Fig. 9.

For our case we will assume the QDs have an ellipsoidal form. Following the
same procedure described earlier for spherical QDs, the following eigenfrequencies can
be determined for ellipsoidal dots$^6$:

$$\frac{\varepsilon_1(\omega_{\text{m}})}{\varepsilon_2(\omega_{\text{m}})} = \frac{\partial}{\partial x} \left[ \frac{\ln Q_{n}^{m}(x)}{\ln P_{n}^{m}(x')} \right]_{x = x' = R_{P}/\sqrt{R_{P}^2 + R_{E}^2}}.$$  \hspace{1cm} (31)

where $Q_{n}^{m}$ are Legendre functions of the second kind, $R_{P}$ is the polar radius of the dot and
$R_{E}$ is the equatorial radius of the dot. The interface modes are determined by substituting
known values of the GaAs and the InAs LO mode, TO mode, and high frequency
dielectric constant $\varepsilon_{\infty}$ into Eq. 28, inserting this result in to Equation 31, and solving for $\omega$. Eq. 31 was solved with Mathematica for several values of $l$ and $m$, see Appendix A.
This resulted in an IF mode value of 220.5 cm$^{-1}$ ($l = 1, m = 0$), corresponding to a mode
found in experiment in both the indented and non-indented areas.
A QD mode was identified at 262 cm\(^{-1}\) off of the pattern. This is in good agreement with the experimentally determined capped InAs/GaAs QD mode identified between 255-258 cm\(^{-1}\) in Ref. 7 and with the calculated mode of 258.9 cm\(^{-1}\) in Ref. 12. On the patterned regions our data reveals another mode at 269 cm\(^{-1}\). The intensity of this mode increased as the pattern spacing decreased (Fig. 10 and Table 2) and as the indent load increased (Fig. 11 and Table 3). As evident by the AFM images of Figure 9, the density of QDs increases as spacing decreases and as load increases. Therefore the increase in intensity of this mode with decreased spacing and increased indent load suggests that it is the QD mode in the nano-indentations. Therefore the QD mode for the patterned areas is shifted approximately 7 cm\(^{-1}\) from the non-patterned QD mode.

2.6 Analysis: Strain Calculation

At the time of this work there are no reports about the strain distribution in spherical or uncapped QDs, therefore we used the strain distribution for InAs/GaAs pyramidal capped QDs, shown in Figure 12\(^{12}\). The hydrostatic and biaxial strain are defined as

\[
\varepsilon_H = \varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}.
\]

\[
\varepsilon_B = 2\varepsilon_{zz} - \varepsilon_{xx} - \varepsilon_{yy}.
\]

Where \(\varepsilon_{xx}\), \(\varepsilon_{yy}\), and \(\varepsilon_{zz}\), are components of the strain tensor.
Fig. 12 QD orientation diagram\textsuperscript{13} and hydrostatic and biaxial strain distribution along the center of a pyramidal QD (Z (001) direction).

Figure 12 shows the hydrostatic and biaxial strain distribution along the center axis of the pyramid. The strain distribution in Fig. 12 shows that the hydrostatic strain distribution for a capped QD does not change considerably within the dot.

In order to calculate the strain in the nano-indented QD structures, we begin with the Hamiltonian for diamond-type semiconductor materials with strain taken into consideration\textsuperscript{14},

\[
\begin{bmatrix}
(p+2q)/6\omega_0 \left( \varepsilon_x + \varepsilon_y + \varepsilon_z \right)

\varepsilon_x

\varepsilon_z

\varepsilon_y

\frac{r}{\omega_0} \varepsilon_x

\frac{r}{\omega_0} \varepsilon_y

\frac{r}{\omega_0} \varepsilon_z

\frac{r}{\omega_0} \varepsilon_x

\frac{r}{\omega_0} \varepsilon_y

\frac{r}{\omega_0} \varepsilon_z

\end{bmatrix}
\]

(33)

where \( p, q \) and \( r \) are deformation potentials that describe changes in restoring force constants and \( \omega_0 \) is the unperturbed bulk frequency.
Equation 33 can be diagonalized for a uniaxial strain along the [001] or [111] directions. This Hamiltonian has three solutions; a singlet frequency with eigenvectors parallel to the strain axis, denoted with an $LO$ subscript, and a doublet frequency with eigenvectors in the plane perpendicular to the strain axis, denoted with a $TO$ subscript. The expressions for the phonon frequency changes due to biaxial strain that follow from this Hamiltonian in zincblende materials are\textsuperscript{9}

\begin{align}
\omega^{TO} &= \omega^{TO}_0 + \Omega_H + \frac{2}{3} \Omega_S \\
\omega^{TO} &= \omega^{TO}_0 + \Omega_H - \frac{1}{3} \Omega_S \\
\omega^{LO} &= \omega^{LO}_0 + \Omega_H - \frac{1}{3} \Omega_S
\end{align}

where $\Omega_H$ and $\Omega_S$ represent the frequency changes due to hydrostatic and shear strain, respectively. Equations 34, 35 and 36 are expressed in terms of the hydrostatic and biaxial strain components as

\begin{align}
\Omega_H &= \frac{p + 2q}{6\omega_0} \varepsilon_H \\
\Omega_S &= \frac{p - q}{4\omega_0} \varepsilon_B
\end{align}

To incorporate the frequency shift observed in our experimental results we rewrite the equations (34)-(36) for the TO and LO frequencies as,
\[
\begin{align*}
\frac{\Delta \omega^{\text{TO}}}{\omega^{\text{TO}}} &= -\gamma \varepsilon^H + \frac{1}{6} \frac{p-q}{\omega^2} \varepsilon^g \\
\frac{\Delta \omega^{\text{TO}}}{\omega^{\text{TO}}} &= -\gamma \varepsilon^H - \frac{1}{12} \frac{p-q}{\omega^5} \varepsilon^g \\
\frac{\Delta \omega^{\text{LO}}}{\omega^{\text{LO}}} &= -\gamma \varepsilon^H - \frac{1}{3} \frac{p-q}{\omega^2} \varepsilon^g 
\end{align*}
\]  

where

\[
\gamma = -\frac{(p+2q)}{6\omega_0^2} 
\]

is known as the Gruneisen parameter and \(\omega_{\text{LO}} (\omega_{\text{TO}})\) is the unperturbed LO (TO) frequency. The coefficients of the hydrostatic and biaxial strain components in the expressions for the change in frequency are known values for different materials. For InAs\(^9\),

\[
\gamma = 0.85, \quad \frac{p-q}{\omega_{\text{LO}}^2} = 0.819, \quad \frac{p-q}{\omega_{\text{TO}}^2} = 1.012
\]

Substituting the values given in Eq. 41 into Eq. 39 we have

\[
\begin{align*}
\frac{\Delta \omega^{\text{TO}}}{\omega^{\text{TO}}} &= -0.85\varepsilon^H + 0.1691\varepsilon^g \\
\frac{\Delta \omega^{\text{TO}}}{\omega^{\text{TO}}} &= -0.85\varepsilon^H - 0.084\varepsilon^g \\
\frac{\Delta \omega^{\text{LO}}}{\omega^{\text{LO}}} &= -0.85\varepsilon^H - 0.068\varepsilon^g
\end{align*}
\]

Using Eq. 42 and the strain distribution in Fig. 12, we are able to determine the TO and LO modes along the QD, as shown in Figure 13. The dotted line in Fig. 13 represents the mode found in Ref. 12 in capped QDs and corresponds well with the QD LO mode calculated with this method.
The LO mode in our experiment, with uncapped QDs was slightly higher (262 cm\(^{-1}\)).

Fig. 13 Wavenumber vs. Capped QD height

We use the experimentally observed shift in the LO phonon frequency (7 cm\(^{-1}\)) of our uncapped QDs, the hydrostatic strain value for capped QDs and Eq. 41 to obtain an expression for the biaxial strain within a patterned area,

\[
\varepsilon_B = -0.57\varepsilon_{QD\; base} \approx 4.30\varepsilon_{B\; (capped)} \tag{43}
\]

This value for the biaxial strain within the uncapped QDs is four times higher than that of capped QDs. This larger strain explains the preferential growth of QDs within the indented areas.
Chapter 3. Conclusions

Nano-indentation is a promising technique for forming predefined patterns of QDs. We have determined the strain that is the origin of the preferential formation of QDs. We found that this strain is approximately four times larger than in non-indentated regions and therefore results in the preferential formation on indented regions. The additional strain promises the creation of QDs with smaller amounts of InAs than the critical quantity of 1.6 MLs. By depositing less than 1.6 MLs of InAs on nano-indentated samples, the QD formation will occur only in the indented areas thus allowing for more organized QD structure which may lead to applications such as photonic crystals and quantum qubits.
References


Appendices
Appendix A: Mathematica Code for the Calculation of Interface Modes

Spherical Approximation
(* Spherical Approximation *)
(* InAs Quantum dots on GaAs *)
Clear[\(\eta, a, b, c, l\)];

Print[];

(* Parameters for InAs quantum Dot *)
\(LO1 = 243; TO1 = 218; \epsilon_1 = 12.25;\)
Print["Quantum dot parameters: \(\omega_{TO} = \), TO1, " cm\(^{-1}\) \(\omega_{LO} = \), TO1, " cm\(^{-1}\) \(\epsilon_\infty = \), \(\epsilon_1\) E\(\eta[l_] := \frac{\epsilon_2}{\epsilon_1} \left(-1 - \frac{1}{\eta[l]}\right);\)
\(a[l_] := \eta[l] - 1;\)
\(b[l_] := LO1^2 + TO2^2 - \eta[l] \ast (TO1^2 + LO2^2);\)
\(c[l_] := \eta[l] \ast TO1^2 \ast LO2^2 - LO1^2 \ast TO2^2;\)
For[\(l = 1, l < 4, l++\),
];
Print[];
For[\(l = 1, l < 4, l++\),
];
Appendix A: (Continued)

Ellipsoidal/Spheroidal Approximation

(* InAs Quantum dots on GaAs *)
Clear[a, b, c, d, r, \(\lambda\), l, m];

Print[];

(* Parameters for InAs quantum Dot *)
LO1 = 243; TO1 = 218; \(\varepsilon\)_1 = 12.25;
Print["Quantum dot parameters: \(\omega_{TO}\) = ", TO1, " cm\(^{-1}\) \(\omega_{LO}\) = ",
LO1, " cm\(^{-1}\) \(\varepsilon_{\infty}\) = ", \(\varepsilon\)_1]

(* Parameters for surrounding GaAs material *)
LO2 = 295; TO2 = 270; \(\varepsilon\)_2 = 10.89;
Print["Barrier parameters: \(\omega_{TO}\) = ", TO2, " cm\(^{-1}\) \(\omega_{LO}\) = ",
LO2, " cm\(^{-1}\) \(\varepsilon_{\infty}\) = ", \(\varepsilon\)_2]

(* Height/Radius *)
R = 7/18;
Print["Height/Radius ratio: ", R]

\(r[1, m, x]\) :=
Evaluate[D[Log[LegendreQ[1, m, 3, x]], x] / 
D[Log[LegendreP[1, m, 3, x]], x]]; 
\(\lambda[1, m]\) := (\(r[1, m, 1/Sqrt[1 - R^2]]\) + 1) / (\(r[1, m, 1/Sqrt[1 - R^2]]\) - 1)
t1 = Table[{m, \(\lambda[1, m]\)}, {m, 0, 1}] // N; 
t2 = Table[{m, \(\lambda[2, m]\)}, {m, 0, 2}] // N; 
t3 = Table[{m, \(\lambda[3, m]\)}, {m, 0, 3}] // N; 
t4 = Table[{m, \(\lambda[4, m]\)}, {m, 0, 4}] // N; 
t5 = Table[{m, \(\lambda[5, m]\)}, {m, 0, 4}] // N;
Appendix A: (Continued)

Print[StyleForm["\nPositive Root", FontWeight -> "Bold"]];
1 = 1;
For[ml = 0, ml ≤ 1, ml++,
    s = (e2 / e1) * r[1, ml, 1 / Sqrt[1 - R^2]] // N;
    a = 1 - s;
    b = s * (LO2^2 + TO1^2) - (LO1^2 + TO2^2);
    c = LO1^2 * TO2^2 - s * (TO1^2 * LO2^2);
    Print["l = 1, m = ", ml, " Energy (cm^-1): ",
            Sqrt[(-b + Sqrt[b^2 - 4*a*c]) / (2*a)]]
]
1 = 2; Print[];
For[ml = 0, ml ≤ 1, ml++,
    s = (e2 / e1) * r[1, ml, 1 / Sqrt[1 - R^2]] // N;
    a = 1 - s;
    b = s * (LO2^2 + TO1^2) - (LO1^2 + TO2^2);
    c = LO1^2 * TO2^2 - s * (TO1^2 * LO2^2);
    Print["l = 2, m = ", ml, " Energy (cm^-1): ",
            Sqrt[(-b + Sqrt[b^2 - 4*a*c]) / (2*a)]]
]
1 = 3; Print[];
For[ml = 0, ml ≤ 1, ml++,
    s = (e2 / e1) * r[1, ml, 1 / Sqrt[1 - R^2]] // N;
    a = 1 - s;
    b = s * (LO2^2 + TO1^2) - (LO1^2 + TO2^2);
    c = LO1^2 * TO2^2 - s * (TO1^2 * LO2^2);
    Print["l = 3, m = ", ml, " Energy (cm^-1): ",
            Sqrt[(-b + Sqrt[b^2 - 4*a*c]) / (2*a)]]
]
Appendix A: (Continued)

Print[StyleForm["\nNegative Root", FontWeight -> "Bold"]];

l = 1;
For[m1 = 0, m1 ≤ l, m1++,
  s = (e2/e1) * r[1, m1, 1/Sqrt[1 - R^2]] // N;
  a = 1 - s;
  b = s * (LO2^2 + TO1^2) - (LO1^2 + TO2^2);
  c = LO1^2 * TO2^2 - s * (TO1^2 * LO2^2);
  Print["l = 1, m = ", m1, " Energy (cm^1): ",
    Sqrt[(-b - Sqrt[b^2 - 4*a*c]) / (2*a)]]
]

l = 2; Print[];
For[m1 = 0, m1 ≤ l, m1++,
  s = (e2/e1) * r[1, m1, 1/Sqrt[1 - R^2]] // N;
  a = 1 - s;
  b = s * (LO2^2 + TO1^2) - (LO1^2 + TO2^2);
  c = LO1^2 * TO2^2 - s * (TO1^2 * LO2^2);
  Print["l = 2, m = ", m1, " Energy (cm^1): ",
    Sqrt[(-b - Sqrt[b^2 - 4*a*c]) / (2*a)]]
]

l = 3; Print[];
For[m1 = 0, m1 ≤ l, m1++,
  s = (e2/e1) * r[1, m1, 1/Sqrt[1 - R^2]] // N;
  a = 1 - s;
  b = s * (LO2^2 + TO1^2) - (LO1^2 + TO2^2);
  c = LO1^2 * TO2^2 - s * (TO1^2 * LO2^2);
  Print["l = 3, m = ", m1, " Energy (cm^1): ",
    Sqrt[(-b - Sqrt[b^2 - 4*a*c]) / (2*a)]]