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# Micro-Raman measurement of strain in silicon nanowires

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## BOSTON UNIVERSITY COLLEGE OF ENGINEERING

Thesis

# MICRO-RAMAN MEASUREMENT OF STRAIN IN SILICON NANOWIRES

by

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B.E., Changsha University of Science and Technology, 2018

Submitted in partial fulfillment of the

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A true master is an eternal student.

Master Yi

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## MICRO-RAMAN MEASUREMENT OF STRAIN IN SILICON NANOWIRES

#### ZHANCHENG YAO

#### ABSTRACT

Crystalline nanostructures such as silicon nanowires (SiNWs) may have residual mechanical stress and strain from the fabrication process, which can potentially impair their reliability as building blocks of Microelectromechanical system (MEMS). The amount of strain may be minuscule, which requires very accurate measurements to determine the strain. Micro-Raman spectroscopy is a work horse tool since it is a simple, fast and nondestructive technique that can be used to assess mechanical strain. However, a precise evaluation of residual strain for nanostructures using micro-Raman spectroscopy requires careful calibrations and theoretical calculations. This thesis describes the interrelations between Raman shift and strain in fabricated silicon nanowires. The calibration methods are used to eliminate the two dominant errors: errors in focusing, and laser heating effects, which can lead to apparent Raman shifts. Finally, the Raman measurement results are discussed and the corresponding residual strain in the [110] direction is calculated. This work is concluded with the discussion of possible causes of strain.

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# List of Abbreviations

CCD	 Charge Coupled Detector
FWHM	 Full Width at Half Maximum
MEMS	 Microelectromechanical Systems
SEM	 Scanning Electron Microscope
SiNW(s)	 Silicon Nanowire(s)

# Chapter 1 Introduction

A nanowire is a structure with the diameter of the order of a nanometer. It can also be defined as a structure whose thickness or diameter is limited to tens of nanometers while its length can be unbounded. Hence, two dimensions that are perpendicular to the direction of length are quantum-confined. Furthermore, nanowires have enhanced surface scattering, high surface to volume ratio and large aspect ratio, which lead to many uncommon mechanical, electrical and optical properties that are different from their bulk counterparts. With these unique properties, nanowires have extensive applications in different domains of research, such as sensor devices (Li et al., 2007), memory switches (Duan et al., 2002), light-emitting diode (Bao et al., 2006).

Besides the aforementioned examples, applications of semiconductor nanowires in microelectromechanical systems (MEMS) as components are prevailing (Brown et al., 2011; Zhang et al., 2011; Behera and Chandra, 2015; Shaby et al., 2015; Tsuchiya et al., 2018). However, excessive residual stress/strain built up in nanowires during fabrication (O'Connor, 1992) results in impairment of reliability and even structural failure (Hsu and Sun, 1998). Thus, nondestructive and precise characterization of mechanical strains is critical for assessments of the reliability of micro-machined structures.

Before this research, our collaborators from E. Alaca's group did a mechanical Young's modulus test for their silicon nanowires sample with different surface areas. They noticed that the Young's modulus is larger in SiNWs with smaller surface area (with shorter length) from their test. However, this phenomenon can be explained by strain since beam in presence of tensile strain has larger Young's Modulus. To verify the existence of residual strain, effective measurements are needed.

To date, X-ray diffraction (Takeuchi et al., 2009) is one of the commonly used methodologies for measuring stress/strain in microscale structure, but the spot size of a laser beam is normally larger than the lateral dimensions of nanowires. Further, bulge tests, wafer curvature measurement, dynamic (resonant) test, passive strain sensors, microbeam bend test (Srikar and Spearing, 2003) are principally applied for measuring MEMS materials with spatial resolution normally exceeding tens of microns.

Using micro-Raman spectroscopy to characterize strain in nanowires is a very favorable technique. Firstly, Micro-Raman spectroscopy is a workhorse tool since it is a simple, fast and nondestructive technique that can be used to measure a plethora of material properties of low-dimensional materials, for instance, silicon microelectronic devices. Secondly, its high spatial resolution allows precise strain distribution characterization especially when strain varied within several microscales in samples.

Despite the advantages, some challenges remain when micro-Raman measurements are applied to nanowires. Most intuitively, objects of the order of tens of nanowires under an optical microscope are nearly invisible, which builds certain obstacles to focusing on desired locations. Additionally, variables including heating effects from laser (Piscanec et al., 2003), surface topographies of nanostructures (Walsh et al., 2008) implicitly affect Raman shifts, which might be misinterpreted as strains, and therefore compromise the accuracy of results.

My work consists of calibrations and micro-Raman measurements of strain in silicon nanowires (SiNWs). Calibrations are done for the purpose of focusing laser spot on favored locations of inconspicuous SiNWs and of eliminating the laser heating effect. Then, Raman spectra of each SiNW are gained and their Raman shifts are characterized as strain.

This thesis is organized as follows: in Chapter 2, we will discuss the theoretical background of Raman scattering and how Raman shifts are related to strain, which is the basis for all the following analysis. Chapter 3 introduces the notations for our sample system and a brief description of the fabrication process, which may cause strain, conducted by E. Alaca's group. Chapter 4 discusses the potential errors that may impair the accuracy of the results and our calibrations to eliminate them. We will cover the experimental method after calibrations part at the end of Chapter 4. The following chapter, Chapter 5, displays the Raman measurement results, discusses the strain analysis and comparison to the mechanical Young's modulus test results from E. Alaca's group. We conclude this work by providing possible reason for residual strain and by justifying the difference between our experimental results and E. Alaca's simulation results.

#### Chapter 2

## Raman Background

Raman spectroscopy is widely used to determine vibrational modes of molecules and to provide structural fingerprints. Before the illustration of my work, it is necessary to explain the general Raman theory since the strain is identified through the analysis of results from Raman spectroscopy. Here we will discuss the concept of Raman scattering to introduce Raman spectroscopy and further the correlation between Raman shift and strain.

#### 2.1 General Theory

Raman scattering is an inelastic scattering of phonons, photons and electrons interaction, which means the kinetic energy of incident light is different from scattered light so as the wavelength or frequency. The difference between frequency (energy) of incident and scattered light is called Raman shift. In Raman spectroscopy, a source of monochromatic laser light is induced on sample surface to interact with phonons and then the scattered light with various frequency is measured by spectroscopy. As a result, chemical structure and identity, stress/strain and other information of sample can be obtained from qualitative and quantitative analysis of Raman spectrum depicted based on scattered light frequency. The relationship among phonon, Raman scattering and Raman shift is the following.

To describe the vibration wave of a lattice, the amplitude  $Q_j$  of a possible vibra-

tional mode j, at position r and given time t, is expressed as (De Wolf, 1996)

$$Q_j = A_j \exp[\pm i(\boldsymbol{q}_j \cdot \boldsymbol{r} - \omega_j t)], \qquad (2.1)$$

where  $A_j$  is a constant,  $q_j$  and  $\omega_j$  is the wave vector and frequency of phonon, respectively. When monochromatic laser light with a frequency  $\omega_i$  is induced on sample in direction of  $k_i$ , the light related electric field E will yield an electric moment P, at position r and given time t, which is given by (De Wolf, 1996)

$$\boldsymbol{P} = \epsilon_0 \chi \boldsymbol{E} = \epsilon_0 \chi \boldsymbol{E}_0 \cdot \exp[\mathrm{i}(\boldsymbol{k}_i \cdot \boldsymbol{r} - \omega_j t)], \qquad (2.2)$$

where  $\epsilon_0$  and  $E_0$  are constants,  $\chi$  is susceptibility. The susceptibility can be a function of vibration that expanded in a Taylor series for each possible vibration mode, which can be expressed as (De Wolf, 1996)

$$\chi = \chi_0 + \left(\frac{\partial \chi}{\partial Q_j}\right)_0 Q_j + \left(\frac{\partial^2 \chi}{\partial Q_j \partial Q_k}\right)_0 Q_j Q_k + \dots$$
(2.3)

From (2.1) and (2.3), we obtain

$$\boldsymbol{P} = \epsilon_0 \chi \boldsymbol{E_0} \cdot \exp[\mathrm{i}(\boldsymbol{k_i} \cdot \boldsymbol{r} - \omega_i t)] + \\ \epsilon_0 \boldsymbol{E_0} A_j \left(\frac{\partial \chi}{\partial Q_j}\right)_0 \cdot \exp[\mathrm{i}(\boldsymbol{k_i} \pm \boldsymbol{q_j}) \cdot \boldsymbol{r}] \cdot \exp[-\mathrm{i}(\omega_i \pm \omega_j) t]$$
(2.4)

The third and higher-order terms of (2.3) are neglected. (2.4) indicates three different frequencies of scattered light from the electric moment  $\boldsymbol{P}$ , where the frequency  $\omega_i$  is of Rayleigh scattering (elastic scattering) and  $\omega_i + \omega_j$ ,  $\omega_i - \omega_j$  is of anti-Stokes and of Stokes Raman scattering, respectively. The schematic of three distinctive scatterings is shown in Figure 2.1. For Stokes Raman scattering, the Raman shift  $\omega_j$  can be defined as (Srikar et al., 2003)

$$\omega_j = \frac{1}{\lambda_i} - \frac{1}{\lambda_s},\tag{2.5}$$



Figure 2.1: Schematic of Rayleigh, Stokes and anti-Stokes scattering.  $\Delta E_i$  and  $\Delta E_s$  is the energy change of phonon through light absorption and remission, respectively.

where  $\lambda_i$ ,  $\lambda_s$  is the wavelength of incident and scattered light, respectively. The subscripts *i* and *s* that will appear later denote incident and scattered light. The Raman spectrum is a diagram of the scattered intensity as a function of the Raman shift that is usually in the unit of cm<sup>-1</sup>.

The scattering efficiency is given by (Srikar et al., 2003)

$$I = C \sum_{j} |\boldsymbol{e}_{i}^{T} \cdot \boldsymbol{R}_{j} \cdot \boldsymbol{e}_{s}|^{2} \qquad j = 1, 2, 3,$$
(2.6)

where C is a constant,  $\mathbf{R}_{j}$ 's are Raman polarizability tensors, and  $\mathbf{e}_{i}^{T}$ ,  $\mathbf{e}_{s}$  are the polarization vectors of light, the superscript T denotes transposed vector. For silicon, the second-rank Raman tensors corresponding to crystallographic directions x = [100], y = [010] and z = [001] are given by (De Wolf, 1996)

$$\mathbf{R_1} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & d \\ 0 & d & 0 \end{pmatrix} \\
\mathbf{R_2} = \begin{pmatrix} 0 & 0 & d \\ 0 & 0 & 0 \\ d & 0 & 0 \end{pmatrix} \tag{2.7}$$

$$\mathbf{R_3} = \begin{pmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

The system defined by these three crystallographic directions is called reference system in this work. By calculating the scattering efficiency for different polarization vectors of incident and scattered light, we notice that not every crystallographic direction of phonon vibration contributes to scattering. For instance, only phonons vibrating in z-direction can be observed for back-scattering from (001) plane. The detailed discussion about the scattering efficiency of our sample will be provided in Chapter 5.

At this point, we have some basic images about Raman spectroscopy so we can discuss the selection rules for Raman scattering. We will discuss the rules for Stokes Raman scattering, which is commonly used.

#### 1) Momentum Conservation:

$$\boldsymbol{k_s} = \boldsymbol{k_i} - \boldsymbol{q_j} \tag{2.8}$$

Considering the wavelengths of incident and scattered light are comparable, we have

$$|\boldsymbol{q_{j\max}}| \approx 2|\boldsymbol{k_i}| \tag{2.9}$$

Our laser source has 532 nm wavelength as of the incident light while the lattice constant of silicon is around 0.5 nm. As a result, the module of  $q_j$  is almost thousands

of times smaller than the dimension of first Brillouin zone and thus only the phonons near  $\Gamma$ -point of the first Brillouin zone are involved in Raman scattering.

#### 2) Energy Conservation:

$$\hbar\omega_s = \hbar\omega_i - \hbar\Omega \tag{2.10}$$

Here  $\hbar\Omega$  is quantized excitation energy. For silicon, every primitive unit cell has two atoms and consequently acoustic and optical phonons can possibly interact with photon. Since  $|q_j|$  is close to  $\Gamma$ -point due to momentum conservation, the acoustic phonon has all but 0 energy and further the excitation of such acoustic phonon to next energy level barely alters the energy of scattered light, which is hard to be identified by Raman shift. Therefore, only optical phonon can be observed due to its finite frequency near  $\Gamma$ -point.

3) Crystal Symmetry: As aforementioned, some phonon modes are unable to induce Raman scattering for silicon. The selection rules can be determined by standard group-theoretical methods (Loudon, 2001) but we will not dig into elaborate derivations.

#### 2.2 Effect of Strain on Raman Shift

Phonon frequencies can change due to the coupling through third or higher order potential terms to strain variations, which is originated from the anharmonicity of crystal lattice. The third-order term is closely related to an intrinsic material property called mode Grüneisen parameter, which describes the derivative of phonon frequency of each possible mode with respect to strain. For an infinitesimal strain  $\varepsilon_{ab}$ , where subscripts a, b = 1, 2, 3 indicate elements of the strain tensor, the mode-Grüneisen parameter can be defined as (Grimvall, 1999):

$$\gamma_{\boldsymbol{q},j}^{ab} = -\frac{1}{\omega_j} \frac{\partial \omega_j}{\partial \varepsilon_{ab}} \tag{2.11}$$

For strained sample, the second order derivative of atomic displacement u from equilibrium position can be written as (Duan and Yang, 2011)

$$\ddot{u}_{\alpha} = -K^{(0)}_{\alpha\alpha}u_{\alpha} - \sum_{ab\beta} K^{(1)}_{\alpha\beta ab}\varepsilon_{ab}u_{\beta},$$

$$K^{(0)}_{\alpha\beta} = \omega_{j0}^{2}\delta_{\alpha\beta} \qquad K^{(1)}_{\alpha\beta ab} = \frac{\partial K_{\alpha\beta}}{\partial\varepsilon_{ab}} \qquad \alpha, \beta, a, b = 1, 2, 3,$$
(2.12)

where  $\omega_{j0}$  is the phonon frequency in absence of strain,  $\delta_{\alpha\beta}$  is Kronecker delta and  $K_{\alpha\beta}$ is an element of the force constant tensor. The second term on the right-hand side of (2.12) is the alteration term of the atomic elastic coefficient. Due to the symmetry of silicon, only three independent  $K^{(1)}$ 's are effective, which can be expressed as (Duan and Yang, 2011)

$$K^{(1)}_{\alpha\alpha\alpha\alpha} = p,$$

$$K^{(1)}_{\alpha\alpha\beta\beta} = q,$$

$$K^{(1)}_{\alpha\beta\alpha\beta} = r,$$
(2.13)

where p, q and r are the phonon deformation potentials (PDP's). (2.12) can be rewritten as

$$\begin{split} \ddot{u}_{1} &= -\omega_{j0}^{2}u_{1} - [(K_{1111}^{(1)}\varepsilon_{11} + K_{1122}^{(1)}\varepsilon_{22} + K_{1133}^{(1)}\varepsilon_{33})u_{1} + (K_{1212}^{(1)}\varepsilon_{12} + K_{1221}^{(1)}\varepsilon_{21})u_{2} + \\ & (K_{1313}^{(1)}\varepsilon_{13} + K_{1331}^{(1)}\varepsilon_{31})u_{3}], \\ \ddot{u}_{2} &= -\omega_{j0}^{2}u_{2} - [(K_{2121}^{(1)}\varepsilon_{21} + K_{2112}^{(1)}\varepsilon_{12})u_{1} + (K_{2211}^{(1)}\varepsilon_{11} + K_{2222}^{(1)}\varepsilon_{22} + K_{2233}^{(1)}\varepsilon_{33})u_{2} + \\ & (K_{2323}^{(1)}\varepsilon_{23} + K_{2332}^{(1)}\varepsilon_{32})u_{3}], \\ \ddot{u}_{3} &= -\omega_{j0}^{2}u_{3} - [(K_{3131}^{(1)}\varepsilon_{31} + K_{3113}^{(1)}\varepsilon_{13})u_{1} + (K_{3232}^{(1)}\varepsilon_{32} + K_{3223}^{(1)}\varepsilon_{23})u_{2} + (K_{3311}^{(1)}\varepsilon_{11} + \\ & K_{3322}^{(1)}\varepsilon_{22} + K_{3333}^{(1)}\varepsilon_{33})u_{3}]. \end{split}$$

$$(2.14)$$

Combining (2.13) and (2.14), we have

$$\begin{bmatrix} (p\varepsilon_{11} + q\varepsilon_{22} + q\varepsilon_{33}) & (r\varepsilon_{12} + r\varepsilon_{21}) & (r\varepsilon_{13} + r\varepsilon_{31}) \\ (r\varepsilon_{21} + r\varepsilon_{12}) & (q\varepsilon_{11} + p\varepsilon_{22} + q\varepsilon_{33}) & (r\varepsilon_{23} + r\varepsilon_{32}) \\ (r\varepsilon_{31} + r\varepsilon_{13}) & (r\varepsilon_{32} + r\varepsilon_{23}) & (q\varepsilon_{11} + q\varepsilon_{22} + p\varepsilon_{33}) \end{bmatrix} \begin{bmatrix} u_1 \\ u_2 \\ u_3 \end{bmatrix} = \lambda_j \begin{bmatrix} u_1 \\ u_2 \\ u_3 \end{bmatrix},$$
(2.15)

with

$$\lambda_j = \omega_j^2 - \omega_{j0}^2$$
  
or  $\Delta \omega_j = \omega_j - \omega_{j0} \approx \frac{\lambda_j}{2\omega_{j0}},$  (2.16)

where  $\Delta \omega_j$  is the change in frequency in presence of strain for possible phonon mode j and  $\lambda_j$  is the corresponding eigenvalue. By resolving (2.15) we can obtain the well-known form for the secular equation:

$$\begin{vmatrix} p\varepsilon_{11} + q(\varepsilon_{22} + \varepsilon_{33}) - \lambda_j & 2r\varepsilon_{12} & 2r\varepsilon_{13} \\ 2r\varepsilon_{12} & p\varepsilon_{22} + q(\varepsilon_{11} + \varepsilon_{33}) - \lambda_j & 2r\varepsilon_{23} \\ 2r\varepsilon_{13} & 2r\varepsilon_{23} & p\varepsilon_{33} + q(\varepsilon_{11} + \varepsilon_{22}) - \lambda_j \end{vmatrix} = 0$$

$$(2.17)$$

Therefore, the correlation between strain and Raman shift can be derived from the secular equation (2.17), which is given in the reference system with x = [100], y = [010] and z = [001] as eigenvectors. However, most microelectronics structures, including our SiNW arrays, are in general oriented along a [110] axis on the (001) surface of the silicon wafer. Therefore, the important strain or stress components can be expected to be oriented along these axes. The sample related strain analysis will be covered in Chapter 5.

# Chapter 3 Fabrication Method

In this chapter, we will discuss the fabrication of our sample done by our collaborators Alaca et al. through a two-step etching process (Tasdemir et al., 2016; Tasdemir et al., 2015). Our sample is made by arrays of double-clamped SiNWs suspended between two 10  $\mu$ m high triangular supports on a silicon wafer. As shown in Figure 3.1, the length of nanowire is oriented in crystallographic direction [110], hence we define x' = [110], y' = [-110] and z' = [001] for sample system. An array of SiNWs is shown



Figure 3.1: Schematic of a SiNW. The height of the nanowire above silicon wafer (blank area in the figure) is roughly 10  $\mu$ m. The length, width and thickness of the nanowire shown in inset is defined in the direction of x' = [110], y' = [-110] and z' = [001], respectively.

in Figure 3.2. SiNWs within the same row have the equal nominal width (in nm) and



Figure 3.2: Optical microscopic image of an array of SiNWs. Numbers at left are nominal width (nm) for each row, and column numbers denote the aspect ratio (length/nominal width)

the ones within the same column have identical aspect ratio (length/nominal width). The nominal widths of SiNWs are from 10 to 80 nm and the aspect ratios are from 10 to 150. Here we use the term "nominal width" rather than "width" considering the natural oxidation of silicon can reduce the actual width of our SiNWs. The thickness of all SiNWs are around 100 nm and thus we assume the thicknesses of all SINWs equals 100 nm.

This fabrication process starts with a p-type, (001) silicon wafer with 525  $\mu$ m thickness. Firstly, a 200 nm thick hydrogen silsesquioxane (HSQ) is spin-coated on the wafer surface with certain pattern that defines the nominal width, orientation of the SiNWs and shape of triangular supports, which is shown in Figure 3.3(a). These patterns are depicted by electron-beam (e-beam) lithography with various exposure dose ranging from 500 to 5900  $\mu$ C · cm<sup>-2</sup>, and each dosing concentration correspond to one array of SiNWs.

The next step is a shallow reactive ion etching process. Here the HSQ layer is



**Figure 3.3:** Process flow for the fabrication of single suspended SiNW. (a) Patterned etching resist produced by electron-beam lithography. (b) Silicon protrusion shaped by shallow reactive ion etching. (c) Low-temperature oxide (LTO) deposition. (d) Removal of LTO from horizontal surfaces. (e) SiNW released from deep reactive ion etching. (f) Disposal of protective layers.

served as an etching masking material. The exposed wafer surface is processed in a inductively coupled plasma etcher in chlorine gas  $(Cl_2)$  environment. As shown in Figure 3.3(b), a silicon protrusion is formed during this etching process.

Following the formation of silicon protrusion, a protective sidewall coating is essential for the second step deep reactive ion etching. For this purpose, a 80 nm thick low-temperature oxide (LTO) film is deposited by low-pressure chemical vapor deposition (CVD) at 425 °C (Figure 3.3(c)). Further, a fluoroform plasma is applied to remove the LTO from horizontal surface, and thus only lateral coating remains (Figure 3.3(d)). Now a deep reactive ion etching is developed to shape and isolate the suspended SiNW shown in Figure 3.3(e). A specific recipe consisting of alternating steps of plasma etching and passivation is optimized to etch 10  $\mu$ m deep trench (Tasdemir et al., 2016). Finally, the protective HSQ and LTO layers are removed by hydrofluoric acid (HF) vapor etching (Figure 3.3(f)).

Although the etching process can make a clean silicon surface, such surface is vulnerable to natural oxidation. The oxidation that happens after fabrication can be a reason to cause strain and we will cover the justifications of this statement in Section 5.3.

# Chapter 4 Calibrations of Raman Measurements

In this chapter, we will discuss two main errors that mostly affects our results, i.e. focusing and optical heating effect from laser. Each section consists of the mechanism of one factor and means to eliminate such error.

#### 4.1 Calibrations on Focusing

The Raman spectral shift induced by topography has been studied by previous works (Walsh et al., 2008; Tishkova and Bacsa, 2012). This mechanism happens when at least one dimension of the structure is smaller than the focal laser spot or edge of the structure is partially covered by the focal spot.



Figure 4.1: Schematic of a micro-spectroscopic system configuration. Colors of ray traces indicate wavelength, where green denotes traces with wavelength  $\lambda_0$  from on-axis (solid green line) and off-axis (dashed green line) SiNW, red denotes trace with wavelength  $\lambda_1$  from on-axis SiNW diffracted by grating, which explains the false spectral shift from off-axis scattered light.

Here we will have a close look at the internal configuration of micro-spectroscopic

system to better understand this feature. A simplified infinity-corrected microspectroscopic system configuration is shown in Figure 4.1. The ray traces qualitatively illustrate the scattered light path inside the system. Rays from on-axis SiNW with wavelength  $\lambda_0$  and  $\lambda_1$  are traced in solid green and red lines, respectively. These traces are uncoupled through the grating and detected at different position on the CCD. Such displacement on the CCD is recorded as a change in wavelength. However, Rays from off-axis SiNW with wavelength  $\lambda_0$  (dashed green light) be mapped on the same position as red solid trace, which will be misinterpreted as the same change in wavelength as well. In our case, such spectral Raman shift can be miscounted as strain while actually it is from physically off-axis position. Therefore, an effective calibration to eliminate such error is critical for the precision of our experimental results.

Another challenge is that when the focal spot is on the top of triangular support, which should be on the same plane as SiNWs, the SiNWs become nearly invisibe as shown in Figure 4.2. The image outlines clear shapes of triangular supports indicating



**Figure 4.2:** Optical microscopic image of an "invisible" SiNW under 100x objective. This SiNW should suspend between the opposites tips of triangular supports.

a good focusing while our actual research objective, i.e. the SiNW, is seemingly disappeared due to its minuscule width. Such technical issue definitely complicate the entire progress of measurement, and hence our calibration means should rely less on the visual indicator from microscope.

The key to solve this problem is to build Raman intensity profiles for each SiNW with respect to y' and z' direction (Figure 4.3). For convenience, we named every



Figure 4.3: Intensity/Stokes peak position profiles for 80-150 (nominal width-aspect ratio) SiNW. (a) Line map image acquisition along y' direction, ranging from -1 to 1  $\mu$ m, 0.1  $\mu$ m/step. The width of grey area is about the FWHM of fitted Gaussian curve of intensity profiles so the data inside such area is acquired within the focal spot. The inset points out the y' and z' direction.(b) Depth series acquisition along -z' direction, ranging from 2 to -2  $\mu$ m, -0.2  $\mu$ m/step.

SiNW "nominal width-aspect ratio", e.g. 80-150 means the SiNW with 80 nm nominal width and 150 aspect ratio. Figure 4.3 is obtained from 80-150. The calibration process is the following:

We started with finding the most focused laser spot visually and then slightly adjusted the focal spot position until we found the highest intensity from quick spectral acquisition. We defined this position as the origin in sample coordinate system for this specific profile. Then we set up a line map image acquisition, which can automatically acquire Raman spectra one by one from points in given spatial range within x' - y' plane. We set the range from -1 to 1  $\mu$ m, which is the default unit in spectroscopy software (WIRE 4.4), in y' direction and acquire a Raman spectrum for every 0.1  $\mu$ m, which is the smallest step the software can automatically move. We may move the focal spot manually for even smaller spatial interval between each data point. However, such procedure can lead to larger error considering the difficulty to quantitatively locate the focal spot by hand. Moreover, our stage is not perfectly fixed so that the stage is slowly drifting due to the gravity, which means we prefer faster procedure, i.e. automatic measurements, to avoid errors. In addition, we only move the stage (sample) rather than the position of focal spot no matter manually or automatically.

Subsequently, we fitted every spectrum to Lorentzian function with linear background and further plotted their fitted intensity and Stokes peak position profiles in terms of corresponding y' axis coordinate. Again, we fitted our profiles in Figure 4.3 to Gaussian function with linear background. The full width at half maximum (FWHM),  $0.390 \pm 0.006 \ \mu$ m, of Gaussian curve of intensity profile can describes the diameter of focal spot well as the following reason: Ideally, the diameter of focal spot should be described by the FWHM of a Gaussian function when it is gathered by the laser beam scanning through a wire with 0 width (like a Dirac delta function). If the wire has finite width, then the FWHM is

$$W = \sqrt{W_0^2 + W_{\text{wire}}^2},$$
 (4.1)

where W and  $W_0$  is the FWHM of Gaussian gathered from wire with finite width and 0 width, respectively,  $W_{\text{wire}}$  is the finite width of wire. For our case, W = 390nm and  $W_{\text{wire}} = 80$  nm, thus the actual diameter should be  $\sqrt{390^2 - 80^2} = 382$  nm, which is close to W. We include 4 data points that are acquired from SiNW within the focal spot by a grey area. These data clearly shows a down-shift of Stokes peak position, which can be explained by Figure 4.1. Considering the off-axis position moves from one side of focal spot to another in Figure 4.1, the CCD will detect the scattered light at varying positions and misinterpret it as the consistent change in Raman shift. Therefore the Stokes peak position will up-shift or down-shift with respect to the coordinate. Outside the grey area, the signal can be a combination of weak contributions from SiNW and back-scattered silicon wafer.

Then, we set up a depth series acquisition, which is similar to line map image acquisition but only move along z' axis. Since the Raman shift variation is not very sensitive in depth acquisition, we extended the rang from 2 to -2  $\mu$ m and set the interval as -0.2  $\mu$ m/step. One may notice that we were going the opposite direction of z', which is intended. Since the stage has a gravitational drift, if we move the stage in z' direction, such drift will offset part of the interval and make the profile looks stretched.

After the series acquisition, we fitted and plotted z'-intensity profile in the same way. Ideally, if the movement is exactly aligned with z' axis away from most focused point, the Stokes peak position should have no apparent shift but only broadening and less intensity. However, the track of stage cannot be perfectly aligned to the laser beam. For instance, we assume the width of SiNW is 80 nm and the angle between the direction of laser beam and stage is 89 °. Once the stage moves  $80/\tan(90 - 89) \approx 4583$  nm, the center of focal spot can already horizontally move from one edge of the SiNW to the other. This is the widest SiNW example for our sample, not to mention even narrower nanowires, which is more sensitive to the tilt of the stage. Therefore, the z' profile shows a similar behave as y' but the contribution of SiNW will gradually diminish when away from the most focused spot. Still, this is also a good indicator to tell us how correctly is the system aligned and how careful should we be to conduct the measurement.

Finally, as soon as we obtained the profiles, we can adjust the focal spot until the spectrum displays the intensity of interest, depending on how accurate we need.

#### 4.2 Calibrations to Eliminate Optical Heating

Considering the tiny dimension compared to bulk materials, SiNW is more sensitive to optical heating from laser. Unfortunately, Raman shift can be affected by heating so that we cannot neglect this error either. The exact temperature dependence of Raman spectra of silicon has been probed (Menéndez and Cardona, 1984; Piscanec et al., 2003; Nikolenko, 2013). Since the goal of this work is not to study the temperature dependence but to avoid it, we will only explain how temperature affects Raman shift.

The classical model Lennard-Jones potential is shown in Figure 4.4. The decrease of repulsive term is larger than the attractive term when the atomic distance increases, which results in an anharmonic potential. Thermal expansion originates from such anharmonicity of atom interactions. If the the potential curve is a parabola, the equilibrium atomic distance is always at  $a_0$  due to the identical inward and outward motion of atom, which will never lead to expansion. On the other hand, potentials like Figure 4.4 present an increase in equilibrium spacing caused by an increase in



Figure 4.4: Schematic of Lennard-Jones potential. Different horizontal line denotes different energy level. The vertical black dashed line refers to the ideal equilibrium atomic distance. The purple dashed line indicates a harmonic potential. The blue dots point to the equilibrium atomic distance for correspondent energy level.

energy. The restoring force F induced by the potential U is

$$F = -\frac{\partial U}{\partial a},\tag{4.2}$$

where a is the atomic spacing. At given energy, the slope of U at  $a_{\min}$  is larger than that at  $a_{\max}$ , thereupon the force is smaller at  $a_{\max}$  and further, the mean velocity is slower bringing higher probability density near  $a_{\max}$ . Consequently, the equilibrium atomic spacing shifts toward  $a_{\max}$  from  $a_0$ . As the energy increases due to heating (temperature rise), the force at  $a_{\max}$  decreases as a more flattened slope and thus the equilibrium atomic spacing increases following the same logic. Besides, the flattened potential yields lower vibrational frequency, so the excitation energy, i.e. Raman shift, is lowered. Therefore, the temperature rise leads to a down-shifted Stokes peak.

Our calibration is based on the assumption that the SiNWs will remain in room temperature for critical irradiation power no matter how long they are under laser illumination. We compared the change in Raman shift in terms of silicon wafer for different irradiation power. To ensure that we have the same Stokes peak intensity for different power, we controlled that the products of power and exposure time are the same for all different power. Ten spectra were taken for each irradiation power and corresponding exposure time on the same nanowire for obtaining standard deviation. We should choose the SiNW with the lowest thermal conduction rate to figure out a ideal irradiation power so that such power is valid for all other SiNWs. We assume the thermal conductivity of air and silicon dioxide is much lower than that of silicon so we dismiss the influence of both substances. Then we assume the native oxide thickness  $\delta$  is 20 Å for all the SiNWs and silicon wafer surface. Now we have the thermal conduction rate

$$\frac{Q}{t} \propto \frac{A}{L} \propto \frac{(W' - 2\delta)T}{L},\tag{4.3}$$

where A, L, W' and T is the cross-sectional area, length, nominal width and thickness of SiNWs. For lower rate, we shall consider the highest aspect ratio (longer length per unit width) 150 firstly. Since  $\delta$  and T are constants, the narrower W' is, the lower rate it has. Therefore, we tested 10-150 to secure a desired power.

We fitted the Raman spectra in Lorentzian function with linear background and plotted the change in Raman shift versus irradiation power in logarithmic scale. As shown in Figure 4.5, the power larger than 8.92  $\mu$ W induces apparent down-shift due to optical heating affect while those changes in Raman shift in smaller power are nearly the same. Empirically, we need at least 1000 counts of intensity to reduce spectrum background signal in order to have a good enough fit. Accordingly, we need more time to acquire such high intensity when we use lower power. Thus, even though



**Figure 4.5:** The change of Raman shift compared to silicon wafer as a function of irradiation power. The grey area include apparent down-shift induced by optical heating effect.

smaller power is plausible, we finally choose 8.92  $\mu$ W as desired power to save time.

So far we have done all the calibrations and we were finally confident to do the measurements to our best precision.

#### 4.3 Experimental Method

Firstly, we should choose a array of SiNWs in good condition. Several arrays of SiNWs with various e-beam exposure dose on the silicon wafer are alternatives to conduct micro-Raman measurement. However, the quality of SiNWs varies for different dosing concentration. The array with 5600  $\mu$ C · cm<sup>-2</sup> dose was selected as our sample since most of the SiNWs are free from crack or fracture.

To characterize strain in SiNWs, we need to obtain the Raman spectra for each nanowire. Here we used InVia confocal Raman micro-spectroscopy (Renishaw Plc.) to conduct *in-situ* measurements. The sample was irradiated by a laser with 532 nm wavelength passing through a 100x objective. The 2400 I/mm grating was used in

order to keep high sensitivity of Raman shift variation. The scatted light diffracted by the grating is detected on a charge coupled detector (CCD) and Raman spectrum is gathered. Ten spectra were taken for each nanowire so that the standard deviation of measurements can be acquired. The Raman shift of each SiNWs was obtained by fitting a Lorentzian function with linear background into the Stokes peak from the Raman spectrum. To measure the presence of strain, we should compare the spectrum with the one from strain-free state. We consider the silicon wafer as nearly strain-free and thus its Raman shift is determined as phonon frequency in absence of strain,  $\omega_{j0}$ . After we calculated the change in Raman shift for each SiNW, strain can be decided via the relations specified in Section 5.2.

#### Chapter 5

## Strain Analysis and Discussion

#### 5.1 Micro-Raman Measurement Results

By using the method mentioned in Section 4.3 with 8.92  $\mu$ W irradiation power, we obtained the micro-Raman measurement shown in Figure 5.1. The spectrum for each



Figure 5.1: (a) Change of Raman shifts of SiNWs in terms of silicon wafer plotted as function of length/width, where width is  $W' - 2\delta$ . Each color represents one column. The smooth dashed curves are not fitted curves but simply leading lines, and the arrows correspond to the direction pointed by the black arrow shown in (b) Corresponding positions of SiNWs. From the bottom row to the top, as the direction pointed by the black arrow, the length/width increases within the same column. The missing SiNWs are either broken or shorter than laser spot diameter.

SiNW and silicon wafer is fitted in Lorentzian function with linear background. The

change in Raman shift is calculated by subtracting the Stokes peak position of SiNW by that of silicon wafer. The red, orange, green and blue dots denote the data from SiNWs with 50, 75, 100 and 150 aspect ratio, respectively. The error bars include the overall standard deviations of SiNWs and silicon wafer results:

$$\sigma = \sqrt{\sigma_{\rm SiNW}^2 + \sigma_{\rm Wafer}^2}.$$
(5.1)

We chose length/width as the variable not because it is a strong geometric dependence but it clearly distinguishes every measured SiNW. In fact, we have not found a close correlated dependence of our results. As one may noticed, some SiNWs are excluded in Figure 5.1(b). These SiNWs are either shorter than laser spot diameter or broken. The comparison between a broken and an unbroken SiNW is shown in Figure 5.2.



**Figure 5.2:** Comparison of the SEM pictures between (a) Broken SiNW (10-75) and (b) Unbroken SiNW (10-100).

#### 5.2 Strain Analysis

Since our sample system (x' = [110], y' = [-110], z' = [001]) is different from reference system (x = [100], y = [010], z = [001]), we shall rotate important physical quantities to sample system and change the corresponding notation for convenience. (2.12) in the sample system can be written as

$$\ddot{u}'_{\alpha} = -K_{\alpha\alpha}^{\prime(0)}u_{\alpha} - \sum_{ab\beta} K_{\alpha\beta ab}^{\prime(1)}\varepsilon_{ab}'u_{\beta}, \qquad (5.2)$$

where the quotes denote elements in the sample system. Any following quotes denote the sample system. The correction  $K'^{(1)}$  can be obtained by rotating the tensor  $K^{(1)}$ to the sample system (De Wolf et al., 1996)

$$K_{1111}^{\prime(1)} = K_{2222}^{\prime(1)} = p', \quad K_{3333}^{\prime(1)} = p,$$
  

$$K_{1122}^{\prime(1)} = q', \quad K_{1133}^{\prime(1)} = K_{2233}^{\prime(1)} = q,$$
  

$$K_{1212}^{\prime(1)} = \frac{p-q}{2}, \quad K_{1313}^{\prime(1)} = K_{2323}^{\prime(1)} = r,$$
  
(5.3)

where

$$p' = \frac{p+q}{2} + r, \quad q' = \frac{p+q}{2} - r.$$
 (5.4)

Substituting (5.3) and (5.4) into (5.2), we have the secular matrix in the sample system (De Wolf et al., 1996):

$$\begin{vmatrix} p'\varepsilon_{11}' + q'\varepsilon_{22}' + q\varepsilon_{33}' - \lambda_j' & (p-q)\varepsilon_{12}' & 2r\varepsilon_{13}' \\ (p-q)\varepsilon_{12}' & p'\varepsilon_{22}' + q'\varepsilon_{11}' + q\varepsilon_{33}') - \lambda_j' & 2r\varepsilon_{23}' \\ 2r\varepsilon_{13}' & 2r\varepsilon_{23}' & p\varepsilon_{33}' + q(\varepsilon_{11}' + \varepsilon_{22}') - \lambda_j' \end{vmatrix} = 0.$$
(5.5)

The strain components in the sample system  $\varepsilon'$  can be calculated using Hooke's law:

$$\varepsilon' = \mathbf{S'}\sigma',$$
 (5.6)

where S' is the compliance tensor in the sample system. This results in (De Wolf et al., 1996)

$$\varepsilon_{11}' = \left(\frac{S_{11} + S_{12}}{2} + \frac{S_{44}}{4}\right) \sigma_{11}',$$
  

$$\varepsilon_{22}' = \left(\frac{S_{11} + S_{12}}{2} - \frac{S_{44}}{4}\right) \sigma_{11}',$$
  

$$\varepsilon_{33}' = S_{12}\sigma_{11}',$$
  

$$\varepsilon_{12}' = \varepsilon_{23}' = \varepsilon_{13}' = 0,$$
  
(5.7)

The Raman tensors in the absence of stress can be transformed by

$$R'_{j} = QR_{j}Q^{T}, \qquad j = 1, 2, 3,$$
 (5.8)

where Q is the rotation matrix from the reference system (unit vectors: (1,0,0), (0,1,0), (0,0,1)) to the sample system (unit vectors:  $\frac{1}{\sqrt{2}}(1,1,0)$ ,  $\frac{1}{\sqrt{2}}(-1,1,0)$ , (0,0,1)) and superscript T denotes the transpose of Q. This results in

$$\boldsymbol{Q} = \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0\\ -\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0\\ 0 & 0 & 1 \end{pmatrix}.$$
 (5.9)

Substituting (5.9) into (5.8), we have

$$\mathbf{R'_1} = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 0 & d \\ 0 & 0 & d \\ d & d & 0 \end{pmatrix}$$

$$\mathbf{R'_2} = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 0 & d \\ 0 & 0 & -d \\ d & -d & 0 \end{pmatrix}$$

$$\mathbf{R'_3} = \begin{pmatrix} d & 0 & 0 \\ 0 & -d & 0 \\ 0 & 0 & 0 \end{pmatrix}$$
(5.10)

and the related phonon polarization unit vectors in sample system are

$$v'_1 = (1, 0, 0), \quad v'_2 = (0, 1, 0), \quad v'_3 = (0, 0, 1).$$
 (5.11)

Now the scattering efficiency (2.6) can be rewritten as

$$I = C \sum_{j} |\boldsymbol{e'}_{\boldsymbol{i}}^{T} \cdot \boldsymbol{R'}_{\boldsymbol{j}} \cdot \boldsymbol{e'}_{\boldsymbol{s}}|^{2} \qquad j = 1, 2, 3.$$
(5.12)

Since polarizer are not applied during measurements, we assume  $e'_i$  is either (1, 0, 0) or (0, 1, 0) in the sample system. Filling into (5.12), we have Table 5.1. As shown

Polarizat	Visible Tensors			
$e_i'$	$e_s'$	$R_1'$	$R_2'$	$R_3'$
(1,0,0)	$(1,\!0,\!0)$	-	-	х
$(1,\!0,\!0)$	(0,1,0)	-	-	-
$(0,\!1,\!0)$	(0,1,0)	-	-	х
$(0,\!1,\!0)$	(1,0,0)	-	-	-

**Table 5.1:** Polarization selection rules for back scattering from (001) surface in the sample system.

in Table 5.1, only  $\mathbf{R}'_{3}$  is visible in the Raman spectrum, which corresponds to longitudinal optical (LO) phonons polarization unit vector  $\mathbf{v}'_{3}$ . Since extra stress was not applied intentionally, the stress is too small to cause a distinct Stokes peak splitting of Raman mode (De Wolf et al., 1996). Thus, it is advisable to consider only LO mode is related to Raman shift in our results. Apparent peak splitting phenomenon can be found in previous works (Ureña et al., 2013).

To analyze which strain component contributes to the change of Raman shift, we need to make an assumption of the residual stress. In the simplest approximation, we assume the stress is only along the length of SiNWs, which is in the direction of  $v'_1$  in the sample system. Accordingly, only  $\sigma'_{11}$  is nonzero, and no shear strain components is yielded. Therefore, (5.5) becomes a diagonal matrix and the eigenvalues can be determined by combining (5.4), (5.5) and (5.7):

$$\lambda_{1}' = \frac{1}{2} \left[ p(S_{11} + S_{12}) + q(S_{11} + 3S_{12}) + rS_{44} \right] \sigma_{11}',$$
  

$$\lambda_{2}' = \frac{1}{2} \left[ p(S_{11} + S_{12}) + q(S_{11} + 3S_{12}) - rS_{44} \right] \sigma_{11}',$$
  

$$\lambda_{3}' = \left[ pS_{12} + q(S_{11} + S_{12}) \right] \sigma_{11}'.$$
(5.13)

The related eigenvectors are still given in (5.11). Since the eigenvectors in the sample system are the same as the ones without stress, the Raman tensors will also not change and are given by (5.10) (De Wolf et al., 1996). According to the selection rules shown in Table 5.1, only  $\lambda'_3$  will be considered. Combining (5.13) and (2.16), we get the change of LO frequency in the sample system:

$$\Delta \omega_3' = \frac{1}{2\omega_0} \left[ pS_{12} + q(S_{11} + S_{12}) \right] \sigma_{11}'.$$
(5.14)

Since the elongations of the SiNWs are of our interest, the equation of  $\varepsilon'_{11}$  in (5.7) is filled into (5.14). This results in

$$\Delta\omega_3' = \frac{2\left[pS_{12} + q(S_{11} + S_{12})\right]}{\omega_0(2S_{11} + 2S_{12} + S_{44})}\varepsilon_{11}'.$$
(5.15)

The Raman shift in the absence of strain  $\omega_0$  is obtained from 10 Raman spectra of silicon wafer. As shown in Figure 5.3,  $\omega_0$  is around 520.53 cm<sup>-1</sup>. To calculate the strain, the elements of compliance tensor and phonon deformation potentials in (5.15) are required. Filling our  $\omega_0$  and the constants of silicon shown in Table 5.2

Elastic Constants			Phonon Deformation Potentials		
(Brantley, 1973)			(Anastassakis et al., 1990)		
S <sub>11</sub>	$S_{12}$	$S_{44}$	p	q	r
$7.68 \times 10^{-12} \text{ Pa}^{-1}$	$-2.14\times 10^{-12}~{\rm Pa}^{-1}$	$12.6\times 10^{-12}~{\rm Pa}^{-1}$	$-1.85 \ \omega_0^2$	$-2.31 \ \omega_0^2$	$-0.71 \ \omega_0^2$

 Table 5.2: Constants of silicon in reference system.



Figure 5.3: Raman spectra obtained from silicon wafer. Colors are used to distinguish different spectrum. The intensity are normalized for each spectrum, and the peak position  $\omega_0$  and its standard deviation are shown on top of the figure.

into (5.15), the relation between change of LO mode Raman shift and uniaxial strain in [110] direction can be obtained:

$$\varepsilon_{11}' = \frac{\Delta \omega_3'}{-388.57 \text{ cm}^{-1}} \tag{5.16}$$

Filling our results shown in Figure 5.1, we can calculate the strain in each measured SiNW. As shown in Figure 5.4, the residual strain is ranging from 0.02 - 0.08%, which is minuscule, and the SiNWs are all under tensile strain. The SiNW with the smallest length/width/surface area for each column shows the largest strain, despite undetermined correlation between strain and size dependence. As mentioned at the very beginning of this thesis in Chapter 1, E. Alaca's group have conducted Young's modulus test for such SiNWs and their results indicate Larger Young's modulus for



Figure 5.4: (a) Strain of measured SiNWs plotted as function of length/width, where width is  $W' - 2\delta$ . Each color represents one column. The smooth dashed curves are not fitted curves but simply leading lines, and the arrows correspond to the direction pointed by the black arrow shown in (b) Corresponding positions of SiNWs. From the bottom row to the top, as the direction pointed by the black arrow, the length/width increases within the same column.

smaller surface area, as shown in Figure 5.5. Since lager tensile strain results in larger Young's Modulus, and our results indicate larger tensile strain for smaller surface area, their mechanical test results coincide with our Raman results.

#### 5.3 Possible Reasons for Strain

As the book (Glas, 2015) mentioned, core/shell heterostructure is one of the reasons for strain. The interface between core/shell causes strain. An interface of two materials with different lattice spacing can induce mismatch. To accommodate such mismatch when two different atoms start to bond with each other, one side of the interface with smaller spacing is under tensile strain and the other side with larger spacing is under compressive strain. The residual strain of our SiNWs can be origi-



Figure 5.5: Elastic modulus (Young's modulus) of SiNWs with different surface area in [110] direction. The measurement results and this figure are from E. Alaca's group.

nated from such heterostructure. After fabrication, the etched surface of our sample is exposed in the air and consequently the natural oxidation happens. Thus, an approximately 20 Å oxides shell is formed as shown in Figure 5.6. Such oxides shell



Figure 5.6: Cross-sectional image of SiNW. The the black area at the center is silicon, and the gray frame is oxide, which construct a core/shell heterostructure. This image is taken by E. Alaca's group.

and silicon core construct a heterostructure and their interface can generate strain. However, we are uncertain if the interface causes a tensile or a compressive strain in silicon core since native silicon oxides are amorphous and consequently the exact lattice spacing is hard to be defined. Therefore, we shall model such structure and predict if the interface induced strain is compressive or tensile. The simulation results gained by E. Alaca's group is shown in Figure 5.7. As the simulation calculated, the



Figure 5.7: Atomistic simulation results from E. Alaca's group. The bottom left inset shows the schematic of a double-clamped silicon nanowire. The top middle is a close-up of the simulated cross-section. The plot at bottom right corner shows the stress in [110] direction versus the positions along the black dashed line on the cross-section.

central area of the silicon core is under around 1 Gpa stress in [110] direction. Since we only have calculated the strain in [110] direction, we shall recalculate the stress in [110] direction to compare with the simulation results. Filling our  $\omega_0$  shown in Figure 5.3 and constants of silicon shown in Table 5.2 into (5.14), we have

$$\sigma_{11}' = -0.435 \text{ cm} \cdot \Delta \omega_3' \text{ GPa.}$$

$$(5.17)$$

Filling our Raman measurement results, we get stress in [110] direction ranging from 0.04 to 0.13 GPa, which is way smaller than the simulation results, around 1 GPa. As shown in Fig.6 and Fig.7 in F. Glas's book (Glas, 2015), page 102, 103, the

ratio of shell thickness, H, to core radius, R, can influence the distribution of strain. Larger H/R induce more strain in the core and vice versa. Since the our sample core (100 × 10 to 100 × 80 nm<sup>2</sup>) is much larger compared to the simulation model's (7 × 7 nm<sup>2</sup>), it is reasonable that our experimental results are much smaller than the simulation results, despite the identical trend of tensile strain shown in both cases.

# Chapter 6 Conclusions

After careful calibrations of measurements, rigorous analysis of experimental results and comparison to simulation predictions, we conclude that the array of SiNWs we measured are all under tensile but minuscule strain in [110] direction, ranging from 0.02 to 0.08%. Thinner nanowires are consistently having a higher strain for a particular nominal length to width aspect ratio. This result supports the conclusion that surface effects from the oxide layer is causing the strain. Also this result explains the Young's modulus increase for smaller surface area, which is due to larger residual strain.

Although plenty of investigations, including edge-enhanced Raman scattering, quantitative temperature dependence of Raman shift, strain analysis under more realistic stress assumption and other factors inducing strain, can be undertook, I am still delighted and proud that I have finally reached to this point in less than one year, given that these accomplishments are built up from my little basis in this domain at the very beginning.

If you decide to continue this research, I recommend you to first understand the theory. Despite the heavy physics and math, plenty of "unusual" phenomena will be transparent if you finally understand them, or at least large part of them. Last but not least, try to enjoy what you are doing and have fun!

## References

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