CATHODOLUMINESCENCE INVESTIGATION OF SEMICONDUCTOR NANOSTRUCTURES

by

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Abstract

The goal of this thesis was to characterize the electronic and optical properties of nanostructured semiconducting materials using cathodoluminescence imaging and spectroscopy in a scanning electron microscope. In particular, two technologically interesting nanostructured semiconductor materials which are believed to exhibit electron confinement effects, porous silicon and $Al_xGa_{x-1}As$ heterostructured nanowires, were studied. Secondary electron and panchromatic cathodoluminescence imaging techniques were used simultaneously to determine the spatial location of specific cathodoluminescence emissions. Room temperature cathodoluminescence spectra from samples of porous silicon were found to exhibit evidence of three-dimensional electron confinement, as well as significant light emission due to $SiO_x$ surface defects originating from the oxidation of the samples during storage in air. Cathodoluminescence spectra of $Al_xGa_{x-1}As$ heterostructured nanowires were collected at temperatures ranging between 293 K and 80 K. These spectra displayed the effects of thermal expansion on the bandgap energy of the material as well as one-dimensional quantum confinement effects in the quantum well regions of the nanowires. In addition, the operating parameters of the scanning electron microscope, such as the beam current, spotsize and beam diameter, were characterized. It was found that the responsivity and signal-to-noise requirements of the cathodoluminescence system prohibited the acquisition of CL for wavelengths greater than 800 nm and it was recommended that a high sensitivity PMT or a Ge near-IR detector be used to perform cathodoluminescence studies in the wavelength range from 700 nm to 1000 nm.
Chapter 1

Introduction

Nanoscience is the study of materials and structures on the order of a billionth of a meter across. At these length scales, between those of the atom and bulk material, novel structural, electronic and optical behaviour can be engineered and observed. One particularly exciting field of nanoscience is semiconductor devices where this unique behaviour can be exploited for the fabrication of higher performance light emitters and detectors, faster electronics and energy conversion.

One reason for the interesting behaviour observed at the nanoscale is the phenomenon of electron confinement. If electrons are confined to move in less than three dimensions, the overall electronic structure of a material changes. For example, electrons can be confined in a material by reducing the physical dimensions to less than the deBroglie wavelength of the electron. In semiconductors this is accomplished by stacking thin layers of materials with differing compositions, thereby forming a “potential well” from which the electrons cannot escape. The effect of confinement on the allowed energy states of an electron in a material can be modeled using quantum mechanics.
One method for investigating the electronic and optical properties of nanostructured materials is by cathodoluminescence (CL) imaging and spectroscopy, where cathodoluminescence is the light emitted when a semiconducting or insulating sample is bombarded by high energy electrons. The wavelength of the light emitted depends on the bandgap energy and allowed electronic transitions for a given material system, and hence, in principle is sensitive to quantum confinement effects as a result of changes of dimension at the nanoscale.

In this thesis, the characterization of technologically interesting microstructured semiconducting materials using cathodoluminescence was performed in a scanning electron microscope. In particular, two nanostructured materials believed to exhibit quantum confinement effects were chosen for study; porous silicon and $Al_xGa_{1-x}As$ heterostructured nanowires. Both of these materials are of importance in the development of the next generation of light emitters and detectors.

The following thesis is divided into 6 parts. Chapter 2 gives a description of the materials studied in this thesis and Chapter 3 outlines the different experimental techniques used to study the materials, which include scanning electron microscopy, panchromatic cathodoluminescence imaging and cathodoluminescence spectroscopy. A discussion of the mechanism of cathodoluminescence and the limitations on resolution and signal strength is given in Chapter 4. Presented in Chapters 5 and 6 are results of the CL study as well as the interpretation of the findings for the porous silicon and nanowire specimens, respectively. In Chapter 7 the conclusions of the research are summarized and several recommendations for future research are offered.
Chapter 2

Description of Material Systems

2.1 Porous Silicon

The microelectronics revolution from which we all benefit everyday is based extensively on high performance silicon technologies [1]. However, the application of bulk silicon to optical devices has been limited to date since silicon is an indirect band gap semiconductor which makes it very inefficient as a light emitter. Consequently, the optoelectronics industry has depended on the use of III-V semiconductors, which are generally expensive to produce and hazardous to handle.

Porous silicon (PS) was first prepared a little more than 50 years ago by A. Uhlir at Bell Labs [2], who observed the unintentional preparation of the material during electropolishing of silicon in HF-based solutions. However, its porous nature was not reported until 1971 by Watanabe and co-workers [3] and most other aspects of the material remained largely uninvestigated during the subsequent 20 years. Broad scientific interest in this material was not initiated until the pioneering work of Canham [4], who in 1990, was the first to report the emission of visible light from PS structures.
The motivation for studying porous silicon is that this material may be used to expand the applicability of silicon to optical devices, in part because it has been shown that as the nanocrystalline grains of silicon (nc-Si) become smaller than a critical value known as the Bohr radius, the efficiency of light emission increases significantly [4]. This is due in part to an effect called quantum confinement, which is believed to affect the energy structure of the material so that the indirect band-gap of the bulk material becomes a direct band gap in the nanocrystals. Another explanation for this increased efficiency could be the reduced number of crystallographic defects in the nanocrystals or the increased importance of surface effects.

Figure 2.1: SEM image of as-prepared porous silicon with a sponge-like porous layer on a silicon substrate.

The term “porous silicon” is used to refer to a variety of nc-Si structures and depending on the fabrication technique or particular production conditions involved, PS thin films may have a variety of different outward appearances. For example, the porous layer may be composed of crystalline silicon particles linked together to form a sponge-like framework with irregularly shaped void spaces, as displayed in Figure
Figure 2.2: SEM image of as-prepared porous silicon sample S1 with low-density crystalline islands on a silicon substrate.

Figure 2.3: SEM image of as-prepared porous silicon sample S3 with closely packed nanoclusters on a silicon substrate.
2.1. Porous silicon may also be produced to form columnar silicon nanostructures. The spaces between these columns form unidirectional channels running perpendicular to the surface of the film, which gives the appearance of pore-like openings at the surface. The name is also applied to crystalline films whose surface is covered with closely packed silicon islands or nanoclusters, each island or nanocluster being composed of porous nanocrystalline silicon grains. This latter variety is displayed in Figures 2.2 and 2.3 and is the type investigated in this thesis.

Porous silicon is often produced by galvanostatic, chemical or photochemical etching of single-crystalline silicon wafers in the presence of HF [1]. However, the PS samples studied in this thesis were fabricated by a novel plasma enhanced hydrogenation technique [5]. The samples were fabricated by S. Mohajerzadeh and his research group at the University of Tehran.

The porous silicon fabrication procedure is illustrated in Figure 2.4. The porous silicon layers were prepared on p-type (100) substrates with a resistivity of 15 \( \Omega \cdot \text{cm} \). The substrates were first cleaned with RCA #1 solution and blown dry in air. A 0.2
µm thick amorphous silicon layer was then deposited by RF-sputtering in an argon atmosphere at a plasma power of 350 W and subsequently placed in a DC-PECVD chamber for three consecutive hydrogenation and annealing steps. The hydrogenation step was performed at different plasma powers and temperatures and the subsequent annealing step was performed at a temperature 70°C higher than the hydrogenation step with the plasma power turned off. The production conditions for the samples studied in this thesis are given in Table 2.1.

In the process of hydrogenation, it is thought that hydrogen radicals replace the dangling bonds of the Si atoms in the amorphous structure. Then, by depassivating these hydrogenated bonds during the annealing step, energy is transfered to the silicon atoms, enhancing the chance of nucleation and growth of nanocrystals. Production of porous silicon by plasma-enhanced hydrogenation could prove to be a superior method compared to the various wet-etching or ion-implantation procedures used conventionally, since this method uses relatively low-temperatures (< 400°C), could be more compatible with existing ULSI manufacturing technologies and might be less costly to integrate into devices [5]. It was found that the particle size distribution and the density of nc-Si islands decreased with increasing the hydrogenation time, that increasing the processing temperature lead to samples with a smaller average grain size and lower plasma power densities resulted in more “packed” structures with a smaller surface size [6]. Since varying levels of quantum confinement result in different emission characteristics, fabrication of porous silicon devices with tunable optical properties by this method is a possibility.
2.2 Semiconductor Nanowires

Semiconductor nanowires are currently attracting considerable scientific attention and various technological applications have been proposed [7]. Heterostructured nanowires may soon be used in the electronics industry as the elements of such devices as bipolar junction transistors and logic gates, single-electron memory devices and pn junction diodes [8]. Other proposed applications for nanowires have been as components of novel biomolecular imaging techniques, waveguides, light-emitting diodes, modulators and even as nanosized heatsinks [9].

Nanowires are needle-like nanostructures which are grown so that they project nearly perpendicular to the surface of the substrate. Secondary electron (SEM) images of as-grown AlGaAs nanowires are displayed in Figures 2.5 and 2.6. They have a diameter of the order of 5 to 50 nm and lengths ranging from a few nanometers to a few microns [10]. This translates into very high aspect ratios of 1000 or more, which is why they are referred to as 1-dimensional quantum materials.

A wide range of methods can be used to synthesize nanowires. Top-down methods include photolithography [11] and selective area epitaxy [12]. There are also bottom-up approaches such as metal-organic vapor phase epitaxy (MOVPE), molecular beam epitaxy (MBE), chemical beam epitaxy (CBE) and laser-assisted growth. All of these methods rely on the catalytic effect of a metal seed particle deposited on the substrate surface for successful growth.

The nanowires studied here were composed of semiconducting materials and grown by gas source molecular beam epitaxy (GS-MBE) at McMaster University by the research group of Dr. Ray LaPierre [13]. This growth method is performed in an ultra-high vacuum environment and allows material deposition to occur slowly, thereby allowing the layers to deposit epitaxially. In the GS-MBE system, group-III species are released as their monomers by heating a solid elemental source and group-V
Figure 2.5: SEM image of as-grown nanowires on the substrate.

Figure 2.6: SEM of as-grown nanowires on the substrate.
species are supplied as dimers from a dual-filament hydride gas cracker operating at 950 °C. When the evaporated elements arrive on the substrate surface, they can react and form crystals.

The nanowires are believed to grow by a vapor-liquid-solid (VLS) process, which requires that the substrates be covered with a thin film of a suitable catalytic material, such as gold. Before the actual growth of the nanowires, the substrate is heated until this layer melts and hemispherically-shaped catalytic “nano-drops” collect on the surface. During epitaxy these liquid metal particles become supersaturated with the source material and this results in preferential precipitation at the metal-solid interface and the growth of a nanosized column of material. Significant growth of the substrate surface occurs simultaneously and therefore the nanowires may be partially buried in a two-dimensional thin film [8].
By stopping the flux from the initial source material and starting another source, the experimenter can grow heterostructured nanowires. In particular, Al$_x$Ga$_{1-x}$As heterostructured nanowires were used in this thesis. The internal structure of these nanowires is illustrated in Figure 2.7. The nanowires have several Al-poor regions (which are labeled W1, W2, and W3) along their length separated by AlGaAs barrier regions (labeled B1, B2 and B3) of a slightly higher Al content. This structure was confirmed using transmission electron microscopy and energy dispersive x-ray spectroscopy methods at McMaster University [13]. In the thinnest of these nanowires the alternating layers of slightly differing compositions are believed to set up several shallow one-dimensional potential wells along the length of the nanowire. Excess carriers (electrons and holes) can be confined in these wells, altering the electronic structure of the region by widening the overall bandgap. Therefore, an observed blue-shift of the peak wavelength of CL emission from the quantum wells compared to that excited from the bulk material may be attributed to one-dimensional confinement effects.
Chapter 3

Investigative Techniques

3.1 Scanning Electron Microscopy

The scanning electron microscope (SEM) is a very popular tool which is used throughout the natural sciences. The instrument located within the Acadia Centre for Microstructural Analysis (ACMA) at Acadia University is a JEOL JSM-5900 LV microscope. In its simplest form, a scanning electron microscope is composed of an evacuated chamber, an electron beam which rasterst across the sample, a grounded sample stage and various electron and photon detectors. The interaction of the electron beam with the sample gives rise to many signals, which can be collected for imaging and spectroscopic analysis. Some of the various detectors available to collect SEM signals include: secondary electron (SE), backscattered electron (BSE), electron beam induced current (EBIC), cathodoluminescence (CL) and characteristic x-rays. These detectors can often be used simultaneously and thus a single instrument can be used to provide structural, compositional, electronic and optical information about a particular sample. Using a secondary electron detector for example, a scanning electron microscope may be used to form a primarily topographical image of the sample at a higher resolution than is achievable using a light microscope.
Figure 3.1 is an illustration of the variety of signals that can be used to produce an image in the SEM [14]. The signals most relevant to this research are secondary electrons and cathodoluminescence.

### 3.2 Cathodoluminescence Spectroscopy

When an electron beam scatters within a material, some of the energy is released in the form of emitted light called cathodoluminescence which depends sensitively on the electronic structure of the material. Cathodoluminescence may be collected and analyzed using a spectrometer and a SEM is a convenient tool which can be equipped with a cathodoluminescence detection system.

#### Serial Spectrometer

The cathodoluminescence system used in this research was a Gatan MonoCL3. A photo of the installed apparatus is shown in Figure 3.2 and a schematic diagram of the system optics is shown in Figure 3.3. This commercial system gathers cathodoluminescence produced in an SEM using a retractable parabolic collection mirror which has a hole through it in in order to allow the electron beam to pass directly though
Figure 3.2: Gatan MonoCL3 cathodoluminescence system installed on the SEM located in ACMA.

Figure 3.3: A diagram showing the path of the light through the Gatan MonoCL3.
to the sample while still allowing secondary electron imaging at a reduced efficiency. The mirror is directly coupled to a chamber mounted Czerny Turner-type high performance monochromator. The entrance and exit slits of the monochromator system can be adjusted using micrometers to balance the requirements of signal strength and spectral resolution. In our system, the user has a choice of two different linear dispersion gratings, a 1200 lines/mm grating and a 600 lines/mm grating which are appropriate for use in the visible and near IR wavelength ranges, respectively. The monochromator is controlled by a stepper motor which allows sequential scanning of a range of wavelengths. Light focused on the exit slit is then directed onto a photomultiplier tube (PMT) interfaced to a computer. Gatan Digital Micrograph™ software allows the visualization and manipulation of CL images and spectra. Stepsize, dwell time and other spectral parameters can be controlled using the software [15].

**Parallel Spectrometer**

Due to the prolonged acquisition times required to acquire spectra of weakly emitting specimens, serial spectrometer systems can be limited in their application to some sensitive types of samples. At the beam energies used in the SEM (0.5-30 keV), it is possible for chemical bonds to be broken and/or rearranged due to the kinetic impact of beam electrons [14], resulting in irreversible beam damage. In addition, prolonged beam exposure can also lead to carbon build-up on the scanned surface [16]. Both of these effects can have a permanent and adverse effect on CL intensity. Since a serial spectrometer works by acquiring a spectrum one wavelength step at a time, there is an unavoidable amount of time required to mechanically adjust the angle of the monochromator grating. In our system, it was found that an extra 103 seconds is added to the active collection time in scanning a wavelength range of 400 nm with a stepsize of 2 nm, which is an extra 0.5 s per step.
One way to shorten the collection time of a spectrum is to collect all the wavelength steps simultaneously rather than acquiring the spectrum one wavelength step at a time (i.e., in parallel rather than serial). This can be accomplished by positioning a linear CCD array after the dispersion grating. All wavelength data is collected simultaneously and hence this type of spectrometer is called a parallel spectrometer.

With the goal of significantly shortening the CL collection time to minimize specimen damage, a parallel spectrometer system based on an Ocean Optics S2000 Miniature Fiber Optic Spectrometer was attached to the original Gatan MonoCL3 apparatus as shown in Figure 3.4. This S2000 Series spectrometer is built to accept light transferred through a fiber optic cable, disperse it with a 600 lines/mm grating, then collect and output the spectrum to a computer. The light is collected from the sample by the same parabolic mirror as in the serial system and then directed upwards and out of the path of the PMT using a plane mirror. A collimating lens positioned inside
a machined housing (shown in Figure 3.5 (a)) was used to couple the light into a detachable fiber optic cable. The alignment of the lens-cable assembly is adjustable using six positioning screws, which allows the user to manually maximize the signal.

In addition, a filter holder attachment (shown in Figure 3.5 (b)) was made to position subtractive filters between the exit beam and the PMT or parallel spectrometer setup. Various ultraviolet, visible or infrared filters can be used to remove unwanted wavelength ranges, which can help to limit spurious noise or remove second order contributions from the CL signal.

**Calibration and Testing of CL Spectrometers**

The performance of the parallel spectrometer was tested against that of the Gatan MonoCL3 using the strong green CL emission from a phosphor particle. CL was excited using a 10 kV electron beam over a wavelength range from 400 to 750 nm using a three second dwell time, which represents three seconds per wavelength step in the case of the serial spectrometer. The serial spectra were recorded using the 600
lines/mm dispersion grating and a stepsize of 2 nm, requiring a total collection time of 11 min 43 s. The stepsize of the Ocean Optics spectrometer is fixed at 0.38 nm due to the particular grating and number of pixels in the CCD and took approximately 4 s to collect.

A plot showing the normalized as-collected phosphor spectra from both the serial and parallel spectrometers is given in Figure 3.6. The most striking feature of this plot is that the peak shapes and positions do not overlap well, indicating that one or both of the two spectrometers may have calibration issues. Therefore, the wavelength response of both of the spectrometers had to be checked, and if necessary, re-calibrated.
Figure 3.7: Measured tungsten lightbulb emission used as reference spectrum as obtained using the calibrated ANDO AQ-6415E Optical Spectrum Analyzer.

A small 9 V tungsten light bulb was used as a “standard” illumination source and a reference spectrum was taken using a calibrated ANDO AQ-6415E Optical Spectrum Analyzer. The ANDO can collect spectra from light coupled through a single or multimode optical fiber over a wavelength range from 350 to 1750 nm [17]. It has a wavelength accuracy of ±0.5 nm, an adjustable resolution ranging from 0.05 to 10 nm and an absolute intensity accuracy of +/- 0.3 dB. The reference spectrum collected using the ANDO is plotted in Figure 3.7.

The emission from this light bulb is approximately that of a blackbody light radiator [18]. Thus, the intensity of the lamp emission, $I$, as a function of the wavelength, $\lambda$, and blackbody filament temperature, $T_B$, can be modeled using Plank’s radiation law

$$I(\lambda, T_B) = \frac{2\pi h c^2}{\lambda^5 (e^{hc/\lambda kT_B} - 1)}$$ (3.1)
In order to determine $T_B$, voltage and current data were measured in the low-voltage regime of the light bulb using a low voltage DC power supply and a digital multimeter. The corresponding resistance vs. voltage curve is plotted in Figure 3.8 and was found to fit to a $2^{nd}$ order polynomial. The cold-resistance of the lamp, $R_{20}$, is the intercept of this plot (i.e., $V = 0$) and was 0.5462 Ω.

An operating voltage, $V_K$, of 5 volts was chosen and the operating resistance, $R_K = \frac{V_k}{I_k} = \frac{5}{0.74} \text{ Ω} = 6.767$ Ω was determined using the observed output current from the DC voltage supply. The following expression was then used to estimate the operating temperature, $T_B$, of the filament [19]

$$T_B = 222.2 \left(\frac{R_K}{R_{20}} - 1\right) + 293$$

(3.2)

Plugging in values yields an operating temperature of $T_B = 2820$ K.
Figure 3.9: Theoretical blackbody curve compared to the reference lamp emission spectrum.

The theoretical blackbody curve was then calculated and is shown in Figure 3.9 along with the experimental data. Examining this plot, there appears to be a slight discrepancy between the data and the blackbody curve which is apparent in the lower wavelength range where the blackbody curve consistently underestimates the observed intensity. This systematic discrepancy arises since the light bulb is not a true blackbody radiator but is rather a graybody radiator. A graybody radiator is a hypothetical body similar to a blackbody radiator except that it absorbs some constant fraction, between zero and one, of all electromagnetic radiation incident upon it. This fraction is called the absorptivity and is independent of wavelength.

The radiation equation may be adjusted for graybody radiation by including an effective emissivity, $\varepsilon_{eff}(\lambda)$, term in equation 3.1. The emissivity of tungsten as a
Figure 3.10: The effective emissivity of tungsten at 2800 K as a function of wavelength [20] and the 10th order polynomial fit to the data.

A graybody corrected filament temperature, $T$, can then be determined by equating the brightness of the graybody with an equivalent blackbody.

$$I_{graybody} = \frac{2\pi h c^2 \varepsilon_{eff}(\lambda)}{\lambda^5 (e^{hc/\lambda kT} - 1)} = \frac{2\pi h c^2}{\lambda^5 (e^{hc/\lambda kT_B} - 1)} = I_{blackbody} \tag{3.3}$$

$$T = \frac{h c}{\lambda k} \ln \left( \frac{1}{\varepsilon_{eff}(\lambda) e^{hc/(\lambda kT_B)}} - 1 \right) + 1 \tag{3.4}$$
Using $\varepsilon_{\text{eff}}(\lambda)$, $T_B$, and the other constants, this equation was solved for $T$, which was found to be 3270 K.

The graybody approximation to the light bulb emission was then calculated and is shown in Figure 3.11. It is observed from this plot that a graybody approximation is superior to a blackbody approximation as quantified by a comparison of the coefficients of determination, $R^2$, of the graybody ($R^2 \approx 0.991$) and the blackbody ($R^2 \approx 0.977$) curves.

The emission from the lamp was then collected using both the Gatan MonoCL3 system (using both the 1200 lines/mm and 600 lines/mm gratings) and the parallel spectrometer and these spectra are displayed in Figure 3.12.
Without even considering that the expected emission should be a graybody-like curve, it is apparent that there is a great deal of variation in the wavelength responsivity between the different spectrometer set-ups. The system response, a measure of the sensitivity of the spectrometer system as a function of wavelength, can be calculated using this data as shown in equation 3.5. The dark counts variable is a measure of the electronic noise inherently present in the detector and can be estimated by recording a spectrum with the lightbulb off.

\[
\text{System Response}(\lambda) = \frac{\text{Experimental Data}(\lambda) - \text{dark counts}}{\text{Graybody Fit}(\lambda)} \quad (3.5)
\]
Figure 3.13: System response curves for the three spectrometer configurations investigated.

The final step is to normalize the system response within the wavelength range of interest so that the maximum response has a value of one. The corresponding system response curves for each of the three spectrometer set-ups are shown in Figure 3.13.

These system response curves reveal information about the wavelength sensitivity which may not be intuitive when looking at the raw spectra and this exercise illustrates the importance of calibrating a spectrometer before using it.

Another interesting point is that the experimentally determined system response for the Gatan MonoCL3 spectrometer with the 1200 lines/mm grating roughly matches the shape of the theoretical responsivity obtained by multiplying the expected responses of the grating with that of the PMT. Using component response data provided by Gatan, a small offset between the experimental and theoretical responsivities was observed as shown in Figure 3.14.
Figure 3.14: Reported and measured system response curves for the Gatan MonoCL3 spectrometer with the 1200 lines/mm grating.

Figure 3.15: Measured and shifted system response curve corrected for a possible error in the blaze angle of the diffraction grating.
However, we have found that by allowing for as little as a 2° error in the blaze angle, $\beta$, of the monochromator, the blaze wavelength, $\lambda_\beta$, which is the wavelength of highest response, can be shifted by up to 70 nm as given by [21]

$$\beta = \arcsin \left( \frac{\lambda_\beta}{2d} \right)$$

(3.6)

where $d$ is the distance between the blaze lines on the grating. A comparison between the shifted theoretical response of our system and the measured response are shown in Figure 3.15. The differences between the two curves may be due to not considering the effects of the other optical components in the spectrometer, such as mirrors, in the path of the light beam. A similar comparison could not be performed for the 600 lines/mm grating since there was no company data available in the required wavelength range.

Once the system response curve within the range of interest has been obtained, the experimental spectra may be calibrated by dividing the raw data by the system response curve

$$\text{Corrected Data}(\lambda) = \frac{\text{Raw Data}(\lambda) - \text{Background Level}}{\text{System Response}(\lambda)}$$

(3.7)

As an illustration, the spectra collected from the phosphor particle were corrected using this method and the results are shown in Figure 3.16.
Figure 3.16: Example phosphor spectra after being corrected for variations in wavelength sensitivity.

After correcting for wavelength responsivity, the overlap of the spectra from the serial and parallel spectrometers has improved. However, they still do not match up perfectly, especially for wavelengths greater than 540 nm. There are at least two possible reasons that may account for this discrepancy. First, the difference between the two spectra could be evidence of beam damage, which may have gradually occurred during collection of the serial spectra. The beam was focused on the particle for at least 15 minutes and this may have suppressed the CL intensity in the later half of the MonoCL spectrum. It is well known that the luminescence efficiency of phosphors can degrade under long beam exposures [22], and a darkening of the secondary electron image in the scanned area, which is normally attributed to carbon contamination, was observed.
Another explanation could be that the collection geometry between the light bulb and phosphor spectra was not exactly the same. In the case of the phosphor spectrum, the light was collected from a point source emitting very close to where the beam hit the sample. When the light bulb calibration spectra was being recorded, it was necessary to place a layer of tin foil over the collection mirror and punch a small hole using a needle directly under the beam exit hole in order not to flood the PMT and to minimize the collection of light from many different angles. However, the hole might not have been small enough to limit all spurious light from being collected. This light may have the effect of offsetting the calculated response curve slightly.

A comparison of the signal-to-noise ratios (SNR) of the raw phosphor spectra revealed that the parallel spectrometer set-up performed better than the Gatan MonoCL3, with a SNR of 185 compared to 100. These results are encouraging. For strong emitters such as the phosphor sample used here, the parallel spectrometer set-up has the potential to deliver a faster and less noisy spectrum. However, the absolute sensitivity of the PMT-based Gatan MonoCL3 system is much higher than that offered by the particular Ocean Optics parallel spectrometer used in this experiment. Therefore, when interested in examining very weak CL signals, the Gatan MonoCL3 system was the better option and was subsequently used for the remainder of this research.
3.3 Panchromatic Cathodoluminescence Imaging

Spatial knowledge of specific cathodoluminescence emissions can provide illuminating clues about the recombination mechanisms responsible for luminescence when studying nanostructures. Many cathodoluminescence systems, including the Gatan MonoCL3 system which was used in this thesis, are equipped with cathodoluminescence imaging software. This software allows the spatial variation of cathodoluminescence intensity, as collected by the PMT, to be correlated with the scan position of the electron beam across the area of interest. Each pixel of the image is assigned a colour which corresponds to the relative intensity of the CL emission detected at that location of the scan. An example of this type of image is displayed in Figure 3.17, which shows both the topographic and CL emission images of defects on a silicon substrate.
Chapter 4

Cathodoluminescence Signal

Formation and Resolution

4.1 General Background

The following is a brief description of the theory of cathodoluminescence (CL) which closely follows that developed by Yacobi and Holt [16].

When electron wavefunctions combine in the formation of a solid, quantum theory says that the discrete atomic or molecular energy levels are split in accordance with the Pauli exclusion principle. In an extended three dimensional crystal this process forms bands of very closely spaced energy states, separated by a forbidden energy gap, $E_g$, known as the bandgap. For semiconductors there is usually a filled valence band and partially filled conduction band at temperatures above absolute zero.

Luminescence is the light emitted when a system in an excited state relaxes to a lower energy state. It has long been recognized that a wealth of scientific information can be obtained by studying luminescence, since its features are largely determined by the electronic and defect properties of the excited substance [23]. In the case of CL,
excitation is provided by a beam of accelerated electrons, which is the “cathode” part of the term. Energy is transferred from the beam electrons to the sample electrons during scattering events by an exchange of kinetic energy. Beam electrons elevate charge carriers in the valence band to excited energy states in the conduction band, leaving behind positively charged holes, as illustrated in Figure 4.1. The relaxation of these excited electrons down to a lower energy state in a process called “radiative recombination” can result in the emission of characteristic luminescence. This light is usually in the visible or near-UV range of the spectrum. Excited electrons may travel a short distance in the crystal, characterized by the electron “diffusion length”, before encountering a hole and recombination of the electron and hole can occur. Along its path the excited electrons may instead relax by falling into lower energy states called “traps” set up in the bandgap, such as those set up by donor or acceptor atoms in doped materials, impurity and defect states, or through quantized vibrational modes of the lattice, called phonons. Such recombination paths are called “non-radiative”.

Figure 4.1: A schematic diagram showing the process of excitation, trapping and recombination of an electron hole pair.
Band edge recombination describes the transition which occurs when an electron in a state at the minimum of the conduction band falls into a state at the maximum of the valence band. In a direct bandgap material, such as GaAs shown in Figure 4.2, the minimum of the conduction band lies directly above the maximum of the valence band in terms of the wavevector, $k$, which is related to the crystal momentum, $\hbar k$. Therefore, band edge recombination in a direct bandgap material occurs without a change in momentum. For an indirect bandgap material such as Si shown in Figure 4.3, the crystal momentum of the conduction band minimum and valence band maximum are not the same. In a transition across the bandgap, momentum is not conserved. Recombination may only occur with the mediation of a third body, such as a phonon or a crystallographic defect. Light emission from indirect bandgap semiconductors is therefore usually inefficient and weak.

**Photoluminescence**

A characterization technique which is very similar to cathodoluminescence and often used to corroborate CL results is photoluminescence. Photoluminescence is light excited from a material using high energy photons and may be collected to produce optical spectra with similar features to a CL spectrum. However, one incident photon
can induce only one excitation and recombination event whereas a 10 kV electron, which is typical of accelerating voltages used in a standard scanning electron microscope, might generate thousands of electron-hole pairs. Therefore, carrier generation rates by electron beam excitation may be orders of magnitude larger than achievable by typical optical excitation [24].

4.2 Temperature Dependence of Luminescence

Many cathodoluminescence studies on microstructured materials are performed at low temperatures in order to increase the emitted CL signal [27]. It is useful for electron microscopes and cathodoluminescence systems to come with the option of installing a “cold stage” which can be used to cool the sample down within the vacuum chamber. Liquid helium (∼5 K) or liquid nitrogen (∼77 K) are often used to cool nitrogen gas or air circulating through a sealed pipe connected to a specially designed sample stage. In this research a liquid nitrogen cooled cold stage system was used to perform cold temperature and temperature dependent cathodoluminescence experiments on Al$_x$Ga$_{1-x}$As heterostructured nanowires.

There are several important factors which make it desirable to perform cathodoluminescence studies at low temperatures. One reason is because there is a significant increase in the intensity of the cathodoluminescence signal with a decrease in temperature. Radiative and non-radiative electron-hole recombination processes compete with each other and an electron beam in the 10 to 20 kV range normally excites all possible recombination channels. The excited electrons and holes will relax via each possible path according to their relative probabilities. Certain processes become more probable depending on such considerations as the mobility of the electrons and the electron-phonon coupling efficiency [27]. Cooling can increase the intensity of radiative recombination due to the “freeze out” of other non-radiative pathways. The likelihood of an electron and a hole finding one another before interacting with the
lattice or a defect is much higher at lower temperatures. This increase in intensity can significantly improve the signal-to-noise ratio, making it possible to observe spectral phenomena not accessible at higher temperatures [27].

Another benefit of performing CL experiments at low temperatures is that spectral peaks become narrower and more defined. A marked decrease in vibrionic coupling of electrons and phonons at colder temperatures makes the energy bands in the sample more defined. In addition, interpretation of cold temperature cathodoluminescence spectra can be more reliable since the individual peaks likely correspond to recombination between well-defined energy levels.

It is often the case that the peak wavelength in the emitted spectrum experiences a shift upon heating or cooling. The direction of this shift and its strength can further reveal information about the processes responsible for the emission, as well as provide additional clues to help differentiate between various recombination paths of similar energies. The empirical Varshni expression [28] is commonly used to represent the temperature dependence of direct bandgaps for many different semiconductors. It is given in equation 4.1 as

$$E_g(T) = E_g(0) - \frac{\alpha T^2}{T + \beta} \quad (4.1)$$

where \(E_g\) is the energy gap at 0 K, and \(\alpha\) and \(\beta\) are constants. The dependence of luminescence intensity on temperature can also be well described by another empirical expression [29]

$$I(T) = \frac{I_o}{1 + C \exp \left( \frac{T}{T_o} \right)} \quad (4.2)$$
where C is a constant independent of T, and the scaling constant \( T_0 \) gives a measure of the system disorder. Furthermore, the rate of electron beam damage, which can be significant in some beam sensitive materials, is generally reduced at low-temperatures.

It was found that good quality secondary electron imaging was much more difficult to perform during a cooling experiment. Expansion and contraction of the lattice can cause significant “drift” of the sample during cooling, as well as movement of the sample stage itself. As a result, secondary electron and panchromatic CL images collected at low-temperatures were blurry and indistinct. Focusing on a particular spot on a sample was difficult, a fact which impaired many attempted studies of the CL from individual nanostructures. Vibration of the sample due to the circulation of \( N_2 \) through the cold stage system may also have been a contributing factor to imaging instability. Therefore, a different experimental set-up would be required in order to simultaneously image specific nanostructures and collect the excited CL effectively. Cold temperature experiments using the current CL system should focus on obtaining good average spectra of the emission from a relatively broad area of the sample, at least several micrometers across.

### 4.3 Resolution and Signal-to-Noise Considerations

In this research, one of the primary objectives was to better understand both the theoretical and experimental limits of the resolution achievable when using cathodoluminescence as an investigative technique. The various limitations due to the particular experimental set-up have been discussed in Section 3.2. High resolution imaging in an SEM is generally performed at low operating voltages and low beam currents to minimize the diameter of the electron beam and spreading of the beam within the sample. The small size of the nanostructures studied in this thesis means we require high resolution imaging. As will be shown in the next subsection, significant beam currents are required to excite sufficient cathodoluminescence to perform CL
measurements using our system. Therefore, when using secondary and panchromatic imaging techniques in tandem, a compromise between the acquisition parameters needed for good imaging resolution and also good CL signal generation need to be found. In this section the theoretical limitations on resolution and signal strength will be discussed by studying both the properties of the excitation (i.e., the electron beam) and the underlying physical processes occurring within the material during the formation of the cathodoluminescence signal.

**Intensity and Signal Strength**

Carriers generated in a semiconductor by an incident electron beam will undergo diffusion, followed by recombination processes, some of which give rise to luminescence. The diffusion of excess minority carriers for continuous irradiation can be described using the differential form of the continuity equation [30]

\[ D \nabla^2 (\Delta n) - \frac{\Delta n}{\tau} + g(r) = 0 \]  

(4.3)

where \( D \) is the diffusion coefficient, \( \Delta n \) is the excess minority carrier density per unit volume, \( \tau \) is the minority carrier lifetime and \( g(r) \) is the generation rate of excess carriers per unit volume. The solution of the continuity equation for an arbitrary generation volume is beyond the scope of this discussion. However, if we assume a spherically symmetric distribution, the solution of the continuity equation is much simpler. The excess carrier density in this case is [30]

\[ \Delta n(r) = C \exp\left(-\frac{r}{L}\right) \]  

(4.4)

where \( C \) is a constant and \( L = (D\tau)^{1/2} \) is the minority carrier diffusion length. The depth distribution, \( \Delta n(z) \), can be obtained from this equation by rewriting
this solution and assuming that the total number of carriers generated per second is $GI_b/e$ where $G$ is number of electron-hole pairs generated per beam electron and is also known as the “generation factor”, $I_b$ is the electron beam current and $e$ is the electronic charge [30]

$$\Delta n(z) = \frac{G I_b}{2 \pi e D} \int_0^\infty \frac{\exp\left(-\sqrt{\xi^2 + z^2}/L\right)}{\sqrt{\xi^2 + z^2}} 2\pi \xi d\xi = \frac{G I_b}{2 \pi e D} \exp\left(-\frac{z}{L}\right)$$  \hspace{1cm} (4.5)

where the integration is over the x-y plane and $\xi$ is a radial coordinate in the plane such that $r^2 = \xi^2 + z^2$.

The intensity of the cathodoluminescence signal, $L_{CL}(r)$, is linearly related to the overall recombination rate, $\frac{\Delta n(r)}{\tau}$. However, only a fraction of the total number of recombination events are radiative. This fraction is given by the radiative recombination efficiency, $\eta = \frac{\tau_{rr}}{\tau}$, were $\tau_{rr}$ is the radiative recombination lifetime. The total CL intensity can be expressed as [30]

$$L_{CL}(r) = \int V f \frac{\delta n(r)}{\tau_{rr}} d^3r$$  \hspace{1cm} (4.6)

where $f$ is a function containing correction parameters for the detection system, absorption and internal reflection. A solution to equation 4.6 may be found by assuming spherical or Gaussian generation volumes. Using equation 4.5, the luminescence intensity in a layer of thickness $dz$ at a depth $z$ is [30]

$$L_{CL}(z)dz \propto \frac{G I_b L \exp(-z/L)dz}{e \tau_{rr} D}$$  \hspace{1cm} (4.7)

The actual number of photons generated per second at a depth $z$ is [30]
\[ L_{CL} = f_D f_A f_R \frac{G I_b \tau}{e \tau_{rr}} \]  

(4.8)

where \( f_D \) is a constant factor which accounts for the efficiency of the CL detection system and \( f_A \) and \( f_R \) take into account the losses due to absorption and internal reflection, respectively. Alternatively, in terms of the radiative recombination efficiency, \( \eta \),

\[ L_{CL} = f_D f_A f_R \frac{G I_b}{e} \eta \]  

(4.9)

This equation assumes there is a linear dependence of \( L_{CL} \) on the beam current, \( I_b \), which is not valid for all materials and GaAs, for example, exhibits a superlinear dependence. A useful empirical relationship describing the dependence of the CL brightness on the electron beam current, \( I_b \), and voltage, \( V \), is of the form [30]

\[ L_{CL} = f \left( I_b \right) \left( V - V_o \right)^m \]  

(4.10)

where \( f \) describes the dependence on the beam current, \( V_o \) is a “dead voltage” and \( 1 \leq m \leq 2 \). The dependence of the beam current is normally assumed to be linear, however non-linear behavior \( \left( L_{CL} \propto I_b^n, 1 \leq n \leq 2 \right) \) has been observed in some materials. The dead voltage reflects the fact that a minimum beam voltage is required for the production of CL. Therefore, in order to increase the CL intensity to meet the signal-to-noise requirements of the system, either the beam current, the beam voltage or both must be increased.
Electron Probe Parameters

When using both spectroscopic cathodoluminescence and cathodoluminescence imaging techniques in tandem, electron beam parameters such as operating voltage and spotsizes (beam currents) must be chosen to satisfy the requirements of both. In addition, the electron probe diameter, $d_p$, arriving at the sample surface is one important parameter limiting the image resolution in an SEM. An estimate of the interdependencies of the beam currents, voltage and the electron probe diameter, will be useful in understanding the resolution limits of panchromatic CL images, as well as in determining the optimum parameters for the collection of CL spectra and secondary electron images. In addition, these estimates can also be applied to modeling the expected intensity of the cathodoluminescence signal, the surface area sampled by the beam as well as the depth of electron beam penetration.

According to Goldstein [14], the electron beam diameter, $d_p$, is mainly a function of the parameters of the electron gun and electron optics used in the instrument. The parameters needed to make an estimate of the $d_p$ are the current density, $j_c$, the optical electron brightness, $\beta$, the probe current, $I_b$, and the aberrations and astigmatisms associated with the magnetic lenses used to form the electron beam.

When enough energy is supplied in the form of heat so that the work function energy barrier of the emitter, $E_w$, is overcome, electrons can escape from the filament of the electron gun into the vacuum. This process is called thermionic emission. The cathode current density, $j_c$, obtained from an emitter by thermionic emission is expressed by the Richardson equation [14]

\[
  j_c = A_c T^2 \exp \left( \frac{-E_w}{RT} \right)
\]  

(4.11)
where \( A_c = 120 \frac{A}{cm^2 K^2} \) is constant for thermionic emitters, \( T(K) \) is the filament temperature in degrees Kelvin, \( E_w \) is the work function of the emitter material and \( k = 8.617343(15) \times 10^{-5} \frac{eV}{K} \) is Boltzmann’s constant. In the case of the SEM at Acadia University, the filament material used was tungsten, for which typical values are \( E_w \cong 4.5eV \) and \( T \cong 2700 K \) [14]. Substituting these values yields a current density \( j_c = 3.4 \frac{A}{cm^2} \) [14].

The electron optical brightness \( \beta \) is the current density per solid angle. For thermionic emitters at relatively high voltages, it is more convenient to use the maximum theoretical brightness, \( \beta_{max} \), which according to Langmuir is given by [14]

\[
\beta_{max} = \frac{j_c e V_o}{\pi k T}
\]  

(4.12)

where \( e = 1.602 \times 10^{-19} \text{ C} \) is the electronic charge and \( V_o \) is the operating voltage. When \( V_o = 10 \text{ kV} \), the operating voltage most commonly used in this research, the Langmuir expression yields a value for the maximum brightness of \( \beta_{max} = 4.7 \times 10^4 \frac{A}{cm^2} \).

The beam current, \( I_b \), was measured using a “Faraday Cup”. A Faraday Cup is a sample stub or conductive container with a small hole in it, so that backscattered and secondary electrons cannot escape. The current which flows from the cup to ground is the total beam current. This current was measured using a Keithley 485 autoranging DC picoameter with an uncertainty of +/- 0.1 pA. The beam current was recorded as a function of aperture diameter, beam voltage and spotsize. The spotsize is a setting on the SEM which controls the excitation of the condenser lens and the beam current at a given voltage and aperture size.

Beam current values were recorded in nA as shown in Figures 4.4, 4.5 and 4.6, which are plotted using a logarithmic scale. An estimate of \( d_p \) can now be made using
Figure 4.4: SEM electron beam currents as a function of voltage and spotsize for Aperture 1.

Figure 4.5: SEM electron beam currents as a function of voltage and spotsize for Aperture 2.
the parameters just compiled. For simplicity, it was assumed that all significant aberrations in the system are caused by the magnetic objective lens of the microscope [14]. Another assumption which greatly simplifies the calculation is that the probe diameter has a symmetrical shape such as a Gaussian intensity distribution. If this assumption is introduced, then the effects of the aberrations on the diameter of the electron beam can be taken into account by adding the effects of various aberration disks in the same way as error functions are added. If \( d_g \) is the Gaussian probe size, \( d_s \) the diameter of the spherical aberration disk, \( d_d \) the diameter of the aperture diffraction disk and \( d_c \) the diameter of the chromatic aberration disk, then \( d_p \) is given by

\[
d_p = \sqrt{d_g^2 + d_s^2 + d_d^2 + d_c^2}
\]  

(4.13)
The final expression, upon substitution of the expressions for each of the terms [14] is

\[
d_p = \sqrt{\frac{4}{\beta \pi^2 \alpha^2} \frac{I_b}{4} + \frac{C_s^2 \alpha^6}{\alpha^2} + \frac{(0.61\lambda)^2}{\alpha^2} + \frac{\Delta E^2 C_c^2 \alpha^2}{E_o^2}} \quad \text{(4.14)}
\]

where \( \alpha \) is the angle of the outermost ray through the objective lens, \( C_s \) is the spherical aberration coefficient, \( C_c \) is the chromatic aberration coefficient, \( \Delta E \) is the energy spread of electrons leaving the filament, \( E_o \) is the beam energy and \( \lambda \) is the electron wavelength.

Using the beam currents as a function of voltage and aperture size as given in Figures 4.4, 4.5 and 4.6, \( \beta_{\text{max}} \) as calculated using equation 4.12 along with typical values for the other parameters (\( \alpha = 5 \text{ mrad}, C_s = 20 \text{ mm}, C_c = 10 \text{ mm}, \Delta E = 3 \text{ eV} \)) [14], a reasonable theoretical estimate of the electron probe diameter as a function beam current was calculated for each aperture.

Figures 4.7, 4.8 and 4.9 show that the relationship between electron probe diameter and beam current is nearly linear for a particular voltage and aperture size. In addition, the beam diameter decreases with increasing operating voltage for a particular value of beam current. The shape of these plots, and the shift with increasing voltage are as expected for tungsten in the range of voltages from 5 to 30 kV [14].

Aperture 2 was used in this work as a compromise balancing the requirements of beam current and imaging resolution. According to Figure 4.3, for a spotsize of 60 and operating voltage of 10 kV, the conditions used for CL spectroscopy in this thesis, the diameter of the beam was estimated to be \( d_p \approx 200 \text{ nm} \). For typical CL imaging conditions, which were a spotsize of 20-25 and operating voltage of 10 kV the diameter of the beam was estimated to be \( d_p \approx 15 \text{ nm} \). This may be considered an approximate lower limit to the resolution. Secondary electron and
Figure 4.7: SEM electron beam diameters as a function of voltage and spot size for Aperture 1.

Figure 4.8: SEM electron beam diameters as a function of voltage and spot size for Aperture 2.
backscatter imaging can achieve better resolution than the lower limit imposed by the beam diameter, since strong absorption of secondary electrons decreases the electron escape volume substantially [14].

### Interaction Volume and Carrier Generation

Since electrons are charged particles, their behaviour in materials is complex. However, the distribution of electron energy dissipation in the solid and the accompanying generation of carriers may be described by a relatively simple combination of inelastic and elastic scattering mechanisms. Elastic scattering of beam electrons by the nuclei of atoms may be analyzed using Rutherford’s model and inelastic scattering can be described by the Bethe expression [16].

However, a useful method for estimating the carrier generation volume in a sample is by Monte Carlo trajectory simulation and the program Casino version 2.42, which
Figure 4.10: A series of Monte Carlo simulations showing the effect of increasing operating voltage on the interaction volume for a sample of silicon. The plots are given for operating voltages of a) 5 kV, b) 10 kV, c) 15 kV, d) 20 kV, e) 25 kV and f) 30 kV. Full scale = 800 nm.

The basic principle of Monte Carlo simulation is that the each electron travels a small distance in a straight line between random inelastic or elastic scattering events. The type of scattering event and the scattering angle calculated at each step of the electron's path is determined using random numbers. The energy loss along the trajectory is calculated until the electron can no longer cause an excitation. When about 1000 or more trajectories are used, a Monte Carlo calculation can be used to accurately visualize the effective beam interaction volume.

Figure 4.10 is a plot of the interaction volume as a function of the SEM operating voltage for silicon and it is observed that as the voltage is increased, beam “spreading” occurs. Therefore, in order to maximize the resolution the incident electron voltage and the beam current (spot size) need to be minimized. However, the cathodoluminescence signal increases with beam voltage and current density. Therefore, in order
to meet the signal-to-noise requirements of the particular system being used, some minimum value of beam voltage and beam current is required. Spectral cathodoluminescence measurements presented in this thesis were collected using a beam energy of 10 keV and spotsizes of 60 and 25 for the nanowire and porous silicon samples, respectively. Spatial CL and secondary electron imaging was performed at a beam energy of 10 keV and a spotsize of 20.

Using the Monte Carlo method the electron beam spreading in samples of nanowires and porous silicon was modeled. Collecting CL from samples of nanowires as-grown on the native substrate is difficult due to other considerations which will be discussed in Chapter 6 and hence they were broken off and laid horizontally on a Si substrate. Beam penetration of a nanowire laying horizontally on a silicon substrate was modeled by defining layers of materials with densities corresponding to the compositional structure of the nanowires. Porous silicon was modeled using the density of crystalline silicon.

The energy dissipation in the samples with both the spectroscopic and imaging conditions are shown in Figures 4.11 and 4.12. Paths indicated in yellow correspond to higher energy events, while blue paths correspond to lower energy scattering events.

While these plots show that most of the energy is being dissipated at the point of impact, there is also significant amount of spreading of the beam in the sample. The interaction volume is nearly spherical, and does not depend strongly on the beam current (spotsize).
Figure 4.11: A Monte Carlo simulation of the interaction volume of a single nanowire with (a) spectroscopic and (b) imaging conditions. The top layer represents the nanowire and the bottom layer is the silicon substrate.

Figure 4.12: A Monte Carlo simulation of the interaction volume of porous silicon with (a) spectroscopic and (b) imaging conditions.

According to these plots, the spreading of the electron beam is slightly less for a sample of nanowires than for crystalline silicon. This is due to the difference in density between the two materials. Due to this beam spreading in the sample and therefore the limitations on the resolution, acquiring CL spectra from individual nanostructures, such as a single nanowire, is difficult.
**Recommendations**

Often, one of the most difficult exercises when working with a piece of equipment or in testing a particular technique is to optimize the parameters leading to a maximum signal efficiency. With reference to collecting cathodoluminescence spectra using the Gatan MonoCL3, the idea was to try and adjust the system in order to maximize the signal-to-noise ratio. One factor which was found to be very important in maximizing the collected signal was the distance of the sample from the paraboloidal collection mirror, the working distance (WD).

In order to gain a sense of the effect of working distance on the observed signal, a sample of geological silicate was used to provide a uniform, high intensity cathodoluminescence emission. The sample was polished flat which made it suitable to use in quantifying the drop-off of the CL signal with separation. The observed count rate was recorded as the sample was moved by increments of half a millimeter away from the parabolic mirror.

The average relative count rate over five trials is given in Figure 7.1. From this plot it was determined that the optimal working distance was approximately 14.5 mm. As expected, the captured signal decreased when the sample was moved either closer or farther away from this optimal position.
Figure 4.13: Average relative change in the count rate with sample working distance over five trials.

The monochromator of the Gatan MonoCL3 has two slits, an entrance and exit slit, which may be adjusted using micrometers. These slits can be used to maximize the input signal, but they also have an effect on the resolution of the spectrometer. The wider the slit, the lower the overall achievable wavelength resolution of the system. In order to estimate the best combination of slit widths for the acquisition of CL signals, a green laser beam (peak wavelength $\sim 535$ nm) was directed into the parabolic mirror and spectra were collected, using the 1200 lines/mm grating, for a variety of combinations of entrance and exit slit widths. The FWHM of the spectral peak was taken to be a measure of the resolution, and the relative intensity of the peak was taken as a measure of the relative amount of signal reaching the detector.
Figure 4.14: The resolution of the monochromator as a function of slit width.

Figure 4.15: The captured signal as a function of slit width.
The results of this experiment shown in Figures 7.2 and 7.3. From these plots it can be shown that if the signal is weak, increasing the entrance slit width has the greatest effect on increasing the collected signal. However, it also has the greatest effect on the resolution. For exploratory work, it is recommended that the entrance and exit slits should be maintained at 3 mm each.

The response of the monochromator gratings used in the Gatan MonoCl3 cathodoluminescence system are given in Figure 7.4.

![Graph showing the response of monochromator gratings](image)

**Figure 4.16:** Relative sensitivity of the monochromator gratings used in the current Gatan MonoCl3 system. Courtesy of Gatan.

According to these plots, the response of the monochromator gratings do not fall to zero after 800 nm. However, the system response, given in Figure 3.13 shows that the total sensitivity does fall close to zero after 800 nm. It was found that this cut-off point was not due to the performance of monochromator but was due to the drop off in the sensitivity of the photomultiplier tube, the Gatan Blue PMT, which comes as the standard PMT installed in the MonoCl system. The response of this PMT
with wavelength is given by the black dataset in Figure 7.5, which shows a drop in response to near zero after 800 nm.

Figure 4.17: Relative sensitivity of the PMT used in the current Gatan MonoCL3 system and a high-sensitivity PMT commercially available. Courtesy of Gatan.

In order to perform measurements of spectra in the near-IR region beyond 800 nm, one solution would be to purchase another PMT with an improved response in this wavelength region. As an illustration, the response of a high-sensitivity PMT also offered for use with the Gatan MonoCl3 system is given by the red dataset in Figure 7.5. However, the use of the high-sensitivity PMT only increases the range of acquisition by another 100 nm. In order to truly perform work in the near-IR region, a Ge detector could be used. An ultra-sensitive germanium detector made by Edinburgh Instruments Ltd. has been purchased and provides high-performance in the near infra-red range of 0.8 - 1.7 µm [40].
In addition, was found that the use of large spotsizes (i.e., high beam currents) of 40 or more was key to increasing the cathodoluminescence signal for weak emitters and were desirable for use in spectroscopic surveys of larger sample regions. For imaging purposes, however, a spotsize of 20-25 is optimal for resolution. Dwell times of 3 to 5 seconds were found to provide good signal-to-noise, although spectra usually take more than ten minutes to collect and beam damage may become a factor.
Chapter 5

Structural and Optical Characterization of Porous Silicon

5.1 Composition and Structural Characterization

Samples of porous silicon fabricated using plasma-enhanced hydrogenation and annealing were studied using transmission electron microscopy (TEM), photoluminescence and Fourier transform infrared (FTIR) spectroscopy. Studies using transmission electron microscopy were performed in a Philips CM30 TEM operated at 300 kV. The results of these studies were previously published [6] and will be summarized here. Figure 5.1 shows bright and dark field TEM micrographs of the porous layer of sample S1. The bright spots in (b) are the nanocrystalline grains and the grain size distribution is given in Figure 5.2. The average grain diameter was approximately 1.9 nm.
Figure 5.3 displays a selected area diffraction pattern taken from a sample of porous silicon [6]. The diffuse ring pattern is characteristic of a polycrystalline material with very small grains. The indexing of the rings resulting from Si planes is shown as 111, 220 and 224, which is confirmation of the crystalline nature of these samples. Fourier transform infrared (FTIR) spectra were taken from these samples [6] indicating the presence of a small amount of Si-O-H bonding, although little or no Si-H bonding was observed.

Figure 5.1: Bright (a) and dark (b) field TEM micrographs recorded from porous silicon sample S1 [6].
Figure 5.2: The grain size distribution diagram of sample S1 [6].

Figure 5.3: A selected area electron diffraction pattern taken from a sample of porous silicon [6].
5.2 Cathodoluminescence Imaging

Cathodoluminescence imaging studies were performed at room temperature using a beam voltage of 10 kV and a spotsize of 20. Results from sample S1 are given in Figures 5.4 and 5.5. These images show roughly round areas of relatively strong light emission, or cathodoluminescence “hot spots”. Similar structures have been reported elsewhere [29] and are unique to CL studies and do not generally appear in spatial photoluminescence studies because of low resolution. Scanning electron images suggest that these hot spots of high CL emission are generated at the surface of the nc-Si nanoclusters distributed over the surface of the sample.
Figure 5.4: Secondary electron (left) and panchromatic CL (right) survey images of porous silicon sample S1.

Figure 5.5: Higher magnification secondary electron (left) and panchromatic CL (right) images of a nanocluster for porous silicon sample S1. CL Spectrum 1 was taken from the bright region.
5.3 Room Temperature Cathodoluminescence

Room temperature cathodoluminescence studies of the spectral region from 350 nm to 900 nm were performed on porous silicon samples using the near-IR grating (600 lines/mm) of the Gatan MonoCL3 system. An accelerating voltage of 10 keV and a spot size of 25 were used. Spectrum 1, shown in red in Figure 5.6, was collected from a “hot spot” on sample S1, whereas 2 and 3 shown in red in Figures 5.7 and 5.8 were collected from regions of differing appearance on sample S3. These spectra were corrected for variations in wavelength responsivity using the method described in Section 3.2.

Figure 5.6: Spectrum 1: As-Collected (red) and responsivity corrected (black) room temperature CL from a single nanocluster of porous silicon from sample S1.
Figure 5.7: Spectrum 2: As-collected (red) and responsivity corrected (black) room temperature CL from porous silicon sample S3.

Figure 5.8: Spectrum 3: As-collected (red) and responsivity corrected (black) room temperature CL from a different region of porous silicon sample S3.
Upon correction, several broad spectral peaks become apparent. These spectra were smoothed using a boxcar average of 3 to make peak fitting easier. The smoothed, corrected spectra are shown in Figures 5.9, 5.10 and 5.11 for spectra 1, 2, and 3, respectively. Spectrum 1, which corresponds to the emission from the edge of a single nanocluster on sample S1, was fit to a single Gaussian peak. The spectra taken from much larger areas, Spectra 2 and 3, were deconvoluted into three Gaussian peaks. Since crystalline silicon has a indirect bandgap of 1.12 eV (1107 nm), any features observed in the spectra are assumed to arise from the structure of the sample or from oxide phases on the sample. The positions of the peaks are summarized in the Table 5.1.

![Smoothed PS Spectrum 1](image)

Figure 5.9: Gaussian peak fit (blue) to Spectrum 1. The spectrum was smoothed using a boxcar filter of size 3.
Figure 5.10: Deconvoluted (grey) and individual (red, green, blue) Gaussian peak fits to Spectrum 2. The spectrum was smoothed using a boxcar filter of size 3.

Figure 5.11: Deconvoluted (grey) and individual (red, green, blue) Gaussian peak fits to Spectrum 3. The spectrum was smoothed using a boxcar filter of size 3.
Table 5.1: Porous Silicon Spectral Peak Positions

<table>
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<th>Spectrum 1 (eV)</th>
<th>Spectrum 2 (λ)</th>
<th>Spectrum 2 (eV)</th>
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Previous spectroscopic studies of porous silicon using cathodoluminescence and photoluminescence have indicated that the appearance of blue, green and red spectral peaks is commonly observed [1]. However, the exact peak positions and the assignment of each peak to a particular recombination mechanism varies. The UV band, although common to all three spectra, is the only peak present in Spectrum 1. From the panchromatic CL images, this emission originated at the surface of the nanoclusters. This UV or sometimes blue emission has been ascribed to a defective oxide phase present on the surface of the nanocrystals [31]. These impurities or defects, most likely SiO$_2$ or Si-O-H bonds, may have been formed during the fabrication process or during subsequent storage in ambient air. These compounds can act as radiative centers for electrons confined in the nanocrystals to escape and recombine preferentially at the surface.

The orange-red and orange-green luminescence bands observed at $\sim 640$ nm and $\sim 585$ nm are believed to be due to quantum confinement effects in the silicon particles [29]. As the nanocrystal size decreases, it is believed that the indirect bandgap of silicon begins to more closely resemble a direct bandgap, and radiative recombination becomes more efficient as a result. It has been reported that a reduction of the size of the silicon nanocrystals can blue shift the main emission, which lies at 1.12 eV in the bulk material [32].
If a nanoparticle is modeled as a three dimensional infinite potential box then the energies of electrons and holes in the first excited state are [33]

\[ E_e = \frac{\hbar^2}{8m_e^*m_oL^2} \]  

\[ E_h = \frac{\hbar^2}{8m_h^*m_oL^2} \]  

where \( L \) is the width of the nanoparticle, \( \hbar \) is Plank’s constant and \( m_e^* \) and \( m_h^* \) are the effective mass coefficients of electrons and holes, respectively in terms of the rest mass of the electron, \( m_o \). The total blue-shift of the bandgap would be on the order of

\[ \Delta E_{Total} = \frac{\hbar^2}{8m_oL^2} \times \left( \frac{1}{m_e^*} + \frac{1}{m_h^*} \right) \]  

The position of the red peak corresponds to a shift of the band gap of \( \Delta E_{red \ peak} = 1.92 \ eV - 1.12 \ eV \cong 0.8 \ eV \). The corresponding shift for the green spectral peak is \( \Delta E_{green \ peak} = 2.12 \ eV - 1.12 \ eV \cong 1 \ eV \). Using values for the reduced masses of electrons and holes in Si, \( m_e^* = 1.18 \) and \( m_h^* = 0.153 \) [32], the diameter of the nanocrystals emitting at these energies should be of the order of

\[ L = \sqrt{\frac{\hbar^2}{8m_o\Delta E_{Total}}} \times \left( \frac{1}{m_e^*} + \frac{1}{m_h^*} \right) \]  

Using \( \Delta E_{red \ peak} = 0.8 \ eV \) and \( \Delta E_{green \ peak} = 1 \ eV \) yields nanocrystal diameters of approximately 1 nm and 2 nm, respectively. This is of the order of the grain size measured from the transmission electron micrographs of sample S1. Therefore, the nanocrystalline grains are small enough for electron confinement to occur and give rise to the observed luminescence peaks.

66
Photoluminescence studies of these porous silicon samples were performed at the University of Tehran. Light emission was excited by an ultraviolet source with a peak wavelength of 248 nm. Figure 5.12 is an optical image of the light coming off the sample. From this image it is clear that the observed photoluminescence correlates qualitatively with the cathodoluminescence observed here. The photo shows that areas of the sample predominantly emit blue, green or red light, which correspond to each of the emissions in the observed CL. The inhomogeneity of the colour across the surface of the sample also agrees with cathodoluminescence observations. For example, the observed ratio of red-to-green emission intensity between Spectrum 2 and Spectrum 3 is significantly different. This may be expected since these spectra were obtained from areas of differing macroscopic appearance and may imply different average nanocluster size. An inhomogeneous distribution of island sizes was observed across the surface of the sample, as illustrated in Figure 5.13 and, as mentioned
previously, nanoparticle size is an important factor determining the efficiency and colour of the CL emission.

Porous silicon samples are known to oxidize very quickly when stored in ambient air. However, the effects of oxidation were not taken into account in the preliminary stages of this project, and so deterioration of the samples made studying the samples using higher beam currents or correlating particular features of the cathodoluminescence spectra to the particular production conditions difficult. In future studies, storage of the samples under vacuum should prolong the time available for effective CL work.
Chapter 6

Structural and Optical
Characterization of Nanowires

6.1 Composition and Photoluminescence

The composition and structure of the AlGaAs heterostructured nanowires were characterized by Dr. Ray LaPierre and his team at McMaster University, where the nanowires were grown. In addition, µ-photoluminescence experiments were conducted at the University of Waterloo and in this section a brief summary of their findings [13] is given.

As discussed in Section 2.2 and illustrated in Figure 2.7, the conical nanowires were grown by GS-MBE and had a “core-shell” type internal structure consisting of several aluminum-rich barrier regions and aluminum-poor well regions spaced along the length of the nanowire. The relative flux of Ga and Al during growth was controlled in order to achieve a nominal well composition of $Al_{0.22}Ga_{0.78}As$ and barrier composition of $Al_{0.52}Ga_{0.48}As$ according to two-dimensional film calibrations. The thickness of the wells were estimated to lie between 4 to 7 nm for the thinnest nanowires and
between 30 to 50 nm for the thickest. Each of the nanowires were estimated to be approximately 100 nm in length.

Using a helium cooled $\mu$-photoluminescence system, where the excitation is provided by a 632 nm HeNe laser, photoluminescence from individual nanowires was collected. Several luminescence peaks at 1.65 eV, 1.68 eV, 1.70 eV and 1.72 eV were observed. The peak at 1.65 eV was tentatively assigned to bulk-like recombination in the $Al_{0.22}Ga_{0.78}As$ regions of the larger nanowires. The higher energy 1.68 eV and 1.70 eV and 1.72 eV peaks, which had much narrower linewidths, were assigned to confinement effects in aluminum poor quantum wells ranging in composition from $x=0.2$ to $x=0.1$. The nanowires were expected to have a composition of $x=0.22$ from two-dimensional film calibrations, but lower than expected compositions may be expected due to the difference in growth mechanisms of nanowires compared to planar films.

### 6.2 Cathodoluminescence Imaging

During the exploratory period of this project, various difficulties in performing CL studies of semiconductor nanowires were encountered. One difficulty was that the narrow diameter of the nanowires was on the order of the diameter of the electron beam which will lead to the sampling of a portion of the substrate as well as the nanowire. The GaAs(111)B substrates on which the nanowires were grown were found to emit a significant background “glow”. The presence of this glow, likely due to recombination at crystal defects on the surface and in the bulk substrate, made distinguishing the signal from the nanowires very difficult. This effect is illustrated in Figure 6.1.
Figure 6.1: Panchromatic CL (left) and SEM (right) images of nanowires and the background “glow” due to recombination from the GaAs substrate.

Figure 6.2: Panchromatic CL (left) and SEM(right) images of a nanowire sample sonicated onto a Si substrate.

Additionally, the electron beam could only sample over a few nanowires at a time since the density of the nanowires on the surface was very low. This was true even when the sample stage was tilted more than 30 degrees, the nanowires did not generate enough light to overcome the GaAs background.
The solution to this problem was to sonicate the nanowire samples in a methanol solution to break the nanowires off the substrate. A small drop (10 µL) of the nanowire suspension was dropped onto a silicon substrate and the methanol suspension was allowed to evaporate off leaving behind the nanowires in dense clusters. These samples provided large numbers of nanowires on a non-emitting background as shown in Figure 6.2.

Spatially resolved cathodoluminescence micrographs of a sample of heterostructured AlGaAs nanowires were collected using the Gatan MonoCL3 cathodoluminescence system. Both secondary electron and CL imaging was performed at room temperature using an accelerating voltage of 10 kV. The imaging was carried out using Aperture 2, a spotsize of 20 and a working distance of 13 mm. These conditions were chosen to yield the best possible secondary electron imaging resolution while also exciting enough luminescence to yield good panchromatic CL image contrast. The sample was brought as close to the pole piece of the SEM as possible to increase light captured by the mirror. Another consideration was that the sample must also be located at the focal length of the mirror, which was found to be ∼1 mm below the edge of the mirror.

Figure 6.3: SEM (left) and panchromatic CL (right) micrographs of a cluster of heterostructured AlGaAs nanowires.
Figure 6.4 shows a tightly packed cluster of nanowires lying horizontally on top of a silicon substrate when imaged using (a) secondary electrons and (b) panchromatic CL. From the panchromatic CL image it is clear that significant CL is emitted from the nanowires. Figure 6.3 shows a group of nanowires at a higher magnification. From these images, the origin of the CL appears to be mainly at the broader end or “base” of the nanowires. One reason for this might be that the electron beam samples a larger relative volume of the nanowire when directed at the base and therefore the CL generation volume is greater. Another explanation, which will be discussed in detail in the next section, is that the most efficient recombination mechanism results in a bulk-like emission from the aluminum-poor regions of the broader nanowires.

6.3 Cold Temperature Cathodoluminescence

A sample of AlGaAs nanowires on a silicon substrate was cooled down to about liquid nitrogen temperature using a cold stage system installed in the scanning electron microscope. The temperature of the sample was controlled by manually adjusting the rate of circulation of cooled nitrogen gas through the system and automatically though the use of an attached heater. Each set point temperature was held con-
Figure 6.5: Cathodoluminescence temperature dependence of nanowires as a function of wavelength.

stant using a PID controller which automatically adjusted the current applied to the heater. The temperature of the stage was measured using a thermocouple and the reading was recorded from a digital display on the PID controller. Upon allowing the temperature of the sample to come to rest at \( \sim 80 \) K, average cathodoluminescence spectra were recorded as the sample was heated back up to room temperature in approximately 20 degree increments. The sample was allowed to rest at each temperature for approximately 10 minutes in order to permit the sample to approach thermal equilibrium. The spectra were collected using a pixel dwell time of 3 seconds in order to achieve an adequate signal-to-noise ratio. A composite plot showing the CL emission as a function of temperature and wavelength is given in Figure 6.5.
Figure 6.6: CL emission from AlGaAs nanowires at $\sim 80 \, K$ displaying two emission peaks.

As the temperature decreased, the intensity of the CL emission increased, while the spectral peak narrowed and blue-shifted slightly. At the coldest temperatures, a shoulder on the left hand side of the main peak became apparent. This spectrum, collected at $\sim 80 \, K$ was deconvoluted into two Gaussian-shaped peaks and replotted in Figure 6.6.

From this fit, it is apparent that there are two separate peaks, one centered at $\sim 730 \, nm$ which will be called Peak 1 and another centered at $\sim 755 \, nm$ which will be called Peak 2. It is believed that the lower wavelength peak, Peak 1, is due to confinement effects in the quantum wells of the thinnest nanowires sampled. The higher wavelength peak, Peak 2, is believed to be due to bulk-like band-edge $\Gamma$ recombination in the aluminum-poor well regions of the larger nanowires, in analogy...
to the account made by LaPierre et al of the observed \( \mu \)-photoluminescence from individual nanowires [13].

In order to confirm these statements, a comparison between theory and experiment will be performed. For ternary alloys such as \( Al_xGa_{1-x}As \), it is generally assumed that the dependence of the bandgap on alloy composition is of a linear or parabolic form. For AlGaAs this is [28]

\[
E_g(Ga_{1-x}Al_x) = (1 - x)E_g(GaAs) + xE_g(AlAs) - x(1 - x)C \quad \text{where}
\]

\[
C = -0.127 + 1.310x \quad 0 < x < 0.45
\]

\[
C = 0.055 \quad 0.45 < x < 1
\]

The AlGaAs \( \Gamma \) valley, the band-edge recombination pathway of interest here, contains features arising from a crossover between the indirect X valley of AlAs and the direct \( \Gamma \) valley of GaAs. An illustration of the band structure of \( Al_xGa_{1-x}As \) in these two regions is shown in Figures 6.7 and 6.8.

According to Vurgaftman [28], \( E^X_g = 2.24 \) eV for AlAs and \( E^\Gamma_g = 1.519 \) eV for GaAs. For the average well composition, \( x = 0.2 \) and the above expression yields a value of

![Figure 6.7: The band structure of \( Al_xGa_{1-x}As \) for \( x < 0.45 \) [34].](image1)

![Figure 6.8: The band structure of \( Al_xGa_{1-x}As \) for \( x > 0.45 \) [34].](image2)
Figure 6.9: Observed shift in the two nanowire peak energies of with temperature.

$E_g^\Gamma(0) = 1.6416 \text{ eV}$, which lies roughly within the spectral region where the efficient luminescence was observed. The average barrier composition, $x = 0.52$, lies past the $\Gamma - X$ crossover point, located at $x = 0.45$ to $0.41$. Therefore, the bandgap in this region is indirect and plugging into the expression above gives $E_g^X(0) = 1.881 \text{ eV}$. This emission should not be readily observed in the luminescence spectra since the efficiency of emission from indirect bandgap materials is far lower than that of direct bandgaps. Indeed, this peak, corresponding to a wavelength of 660 nm, lies well within the optimal range of the detector but was not observed.

Therefore, it is likely that both of the observed emissions are linked to the $\Gamma$ valley bandgap of the $Al_{0.22}Ga_{0.78}As$ region of the nanowires. Figure 6.9 shows the experimental variation of Peak 1 ($\sim 1.7 \text{ eV}$) and Peak 2 ($\sim 1.64 \text{ eV}$) as a function of temperature.
The variation of the Γ valley energy gap of bulk AlGaAs with temperature is expected to fit the empirical Varshni expression [28]. Additionally it will be assumed that the fitting parameters for Al$_x$Ga$_{1-x}$As may be approximated by a linear interpolation between the fitting parameters for the binary compounds GaAs and AlAs, using the composition, x, as the weighting factor.

As discussed in Chapter 2, the heterostructured layers of slightly varying Al composition set up potential barriers analogous to one dimensional quantum wells. If a finite square well geometry is assumed as illustrated in Figure 6.3, the temperature dependence of the depth of the potential well, $V_o(T)$, can be estimated as

$$V_o(T) = \frac{E_{g2}(T) - E_{g1}(T)}{2}$$  \hspace{1cm} (6.1)
where subscripts 1 and 2 are used to denote the well \((Al_{0.2}Ga_{0.8}As)\) and barrier \((Al_{0.52}Ga_{0.48}As)\) compositions, respectively. Using the Varshni expression to model the temperature dependence of the bandgaps, equation 6.1 becomes

\[
V_{o}(T) = \frac{1}{2} \left( E_{g2}(0) - E_{g1}(0) + T^2 \left( \frac{\alpha_1}{T + \beta_1} + \frac{\alpha_2}{T + \beta_2} \right) \right) \quad (6.2)
\]

The most efficient recombination path observed at this wavelength occurs between the conduction and valence band edges. The energy positions, \(E_n\), of the band edges are also modified by confinement effects. Therefore, the approach shall be to solve the time-independent Schrödinger equation for a finite square well potential

\[
V(x) = \begin{cases} 
0 & -a \leq x \leq a \\
V_{o}(T) & \text{otherwise}
\end{cases}
\]

where \(a\) is half the width of the well and the well depth is given by \(V_o(T)\). Finding the solutions of the finite square well problem, the energy eigenvalues \(E_n\), is difficult to perform since the resulting expressions are transcendental. However, an approximate form of the solution can be written as \([35]\)

\[
z_n \approx \frac{\pi}{8z_o} \left( 4(n-1)z_o - \pi + \sqrt{(4z_o + \pi)^2 - 8\pi n z_0} \right) \quad (6.3)
\]

where \(z_n = \frac{a}{\hbar} \sqrt{2mE_n}\) and \(z_o = \frac{a}{\hbar} \sqrt{2mV_o}\). The effective mass parameters for electrons and heavy holes in AlGaAs are \(m_e^* = 0.067\) and \(m_h^* = 0.082\), respectively \([32]\), and were used to calculate the valence and conduction \(n = 1\) energy states (i.e., first excited energy state). The sum of the first excited states of the conduction band-edge electrons and the valence band-edge holes defines the total band edge gap shift.
due to confinement effects and is plotted along with the experimental data in Figure 6.11.

The effect of confinement of the electrons, according to this model, is to blue-shift the bulk peak by roughly 0.002 eV. The inclusion of the temperature dependence in the potential was found to have a small effect on the shift due to confinement. The depth of the potential was relatively shallow since the compositions of the barrier and well were similar. The thermal effect introduced a tiny perturbation which caused the shift due to confinement to decrease by a negligible amount at higher temperatures. The shift due to quantum confinement was found to consistently over estimate the observed peak energies.

Another important effect which was considered was the dilation of the crystal with temperature. Since the band structure is a function of the crystal lattice spacing,
this factor must contribute to the observed energy position of the band states [36].

Typically, this effect amounts to 20 to 50% of the total temperature dependance. The variation of the band-gap energy with temperature induced by thermal expansion, \( \Delta E_{th}(T) \), is given by

\[
E_{th}(T) = -B \left( \frac{\partial E}{\partial P} \right)_T \int_0^T \alpha_{th}(T) dT
\]

where \( B \) is the bulk modulus, \( \left( \frac{\partial E}{\partial P} \right)_T \) is the pressure induced band-gap shift and \( \alpha_{th}(T) \) is the linear thermal expansion coefficient [37]. Using standard polynomial interpolations between the properties of GaAs and AlAs for \( B \) and \( \left( \frac{\partial E}{\partial P} \right)_T \) [38], and using \( \alpha_{th}(T) \) for GaAs [39], the lattice dilation induced bandgap shift was calculated. As shown in Figure 6.3, this effect, if considered on its own, was found fit well to the experimental behavior of the lower energy peak, Peak 2. Therefore, we may have some confidence in assigning this peak to band-edge recombination in the Al poor regions of the larger nanowires.

The next step was to consider both quantum confinement and thermal expansion effects. The total bandgap variation with temperature due to both quantum confinement and thermal expansion correlated very well to the experimental behavior of the higher energy peak, Peak 1, as can be seen in Figure 6.11.

The endpoints of each of the calculated curves reproduced the experimental results very closely. These were the temperatures where the system was allowed to rest for a much longer time than 10 minutes. Therefore, the observed variations in the bandgaps at the other temperatures might be a result of not waiting long enough to reach thermal equilibrium at the specimen, even though the thermocouple reading of the stage indicated the temperature had settled.
Figure 6.12: Thermal broadening of nanowire spectral peaks as quantified by an increase in the FWHM of the peaks.

There are many other effects which might be taken into account such as the contribution from electron-phonon interactions [36] and a shift due to the presence of strain in the lattice. However, these effects are relatively small compared to the contributions just discussed and will not be considered in further detail here.

The full width of the two spectral peaks measured at the half maximum point (FWHM) were found to be $\approx 54$ nm and $\approx 32$ nm for Peaks 1 and 2, respectively. The temperature dependence of the peak width is given in Figure 6.12.

Although the peaks exhibited a slight broadening due to thermal effects, they are wider than expected at all temperatures. Generally, peaks due to confinement related effects are much narrower than bulk-like band-edge emissions since the electron energy states become more defined and separated in the potential well. However, the broadness of these peaks may be due to a couple of factors. The spectra were collected by averaging over an area covered with nanowires with a density similar to that
shown in Figure 6.2. Therefore, the total observed spectrum was a superposition of the simultaneous emission from hundreds of nanowires. Each individual nanowire has a slightly different thickness, which in turn corresponds to a population of slightly different sized quantum wells. In addition, it is expected that in the very narrow barrier and well regions, there might be small variations in the Al content. Since the position of the peak wavelength is a very strong function of the depth and width of the potential well, it is assumed that the total observed emission was a superposition of emissions with slightly differing central wavelengths. The observed spectral peak likely corresponds to the average nanowire thickness and aluminum composition.
Chapter 7

Conclusion

In this thesis, both porous silicon and $Al_xGa_{1-x}As$ heterostructured nanowires were found to emit substantial cathodoluminescence signals which were successfully collected using both imaging and spectroscopic techniques. It was also found that the features of the cathodoluminescence spectra could be adequately explained using quantum theoretical arguments.

At room temperature, porous silicon fabricated by plasma-enhanced hydrogenation was found to exhibit three luminescence peaks at $\sim 400$ nm, $\sim 585$ nm and $\sim 640$ nm, the first of which could be attributed to $SiO_x$ surface defects and the latter two by electron confinement in three dimensions.

A low-temperature cathodoluminescence study was performed on $Al_xGa_{1-x}As$ heterostructured nanowires, which exhibited two luminescence peaks at $\sim 720$ nm and $\sim 755$ nm. When the thermal expansion effects on the bandgap were taken into account, the peaks were attributed to band-edge recombination in the Al-poor regions of the nanowires and a blue-shifted band-edge recombination peak due to electron confinement in one-dimension.
These results indicated that successful cathodoluminescence studies on nanostructured materials could be performed using the equipment available at Acadia University and that spectroscopic cathodoluminescence can be used to reveal important information about the electronic structure of the samples.
Appendix A

Electron Beam Diameter vs. Spotsize

Table A.1: Aperture 1 - Beam Diameters

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Table A.3: Aperture 3 - Beam Diameters

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Bibliography


