Construction and Passive Q-Switching of a Ring-Cavity Erbium-Doped Fiber Laser Using Carbon Nanotubes as a Saturable Absorber

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Construction and Passive Q-Switching of a Ring-Cavity Erbium-Doped Fiber Laser
Using Carbon Nanotubes as a Saturable Absorber

A Thesis
Submitted to the Faculty
of
Rose-Hulman Institute of Technology

by

Austin Murphy Scott

In Partial Fulfillment of the Requirements for the Degree
of
Master of Science in Optical Engineering

August 2017

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ROSE-HULMAN INSTITUTE OF TECHNOLOGY
Final Examination Report

Austin M. Scott  Optical Engineering  Graduate Major

Thesis Title: Construction and Passive Q-Switching of a Ring-Cavity Erbium-Doped Fiber Laser Using Carbon Nanotubes as a Saturable Absorber

DATE OF EXAM: August 10, 2017

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Construction and Passive Q-Switching of A Ring-Cavity Erbium-Doped Fiber Laser Using Carbon Nanotubes as a Saturable Absorber

Thesis Advisor: Dr. Sergio C. Granieri

The purpose of this thesis is to design, build, test, and achieve pulsed operation of a ring-cavity erbium-doped fiber laser using carbon nanotubes as a saturable absorber. The erbium-doped fiber is characterized first, cross-sections are calculated, and the gain value is determined. Subsequently, the ring cavity is constructed and the laser is operated in the continuous wave regime. Much time is then spent trying to characterize and utilize the carbon nanotubes successfully. Many dispersions are made using multiple solvents and dispersing media, various images are taken with both scanning electron and Raman microscopy, and attempts at purification are made. Saturable absorbers are then created both by coating the end facet of a fiber with a dispersion containing carbon nanotubes and by inserting a fabricated poly-methyl-methacrylate (PMMA) and single-walled carbon nanotube (SWCNT) polymer composite film between two fiber end facets. Once inserted into the cavity, the saturable absorbers passively Q-switch the laser in three distinct cases. A fiber end facet coating of SWCNTs dispersed into isopropanol produced pulses with duration
of 17.45 ± 0.11 µs and 2.74 ± 0.14 µs, with repetition rates of 25.36 ± 0.53 kHz and 37.77 ± 0.33 kHz, respectively. A second fiber end facet coating of SWCNTs dispersed into dimethylformamide (DMF) produced pulses with duration of 12.28 ± 1.08 µs and 3.58 ± 0.12 µs, with repetition rates of 25.13 ± 0.63 kHz and 26.46 ± 0.13 kHz, respectively. The PMMA plus SWCNT polymer composite film produced pulses of 0.716 ± 0.007 µs duration and 142.8 ± 1 kHz repetition rate.

Keywords: fiber laser, erbium doped fiber, single-walled carbon nanotubes, saturable absorber, Q-switching
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## LIST OF ABBREVIATIONS

### Laser and Fiber Optic Components and Terminology Abbreviations

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<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>ASE</td>
<td>Amplified Spontaneous Emission</td>
</tr>
<tr>
<td>CW</td>
<td>Continuous Wave</td>
</tr>
<tr>
<td>FC/PC</td>
<td>Fiber Connector / Physical Contact</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full-Width at Half-Maximum</td>
</tr>
<tr>
<td>EDF</td>
<td>Erbium-Doped Fiber</td>
</tr>
<tr>
<td>EDFL</td>
<td>Erbium-Doped Fiber Laser</td>
</tr>
<tr>
<td>Er110</td>
<td>Specific Erbium fiber used as laser gain medium</td>
</tr>
<tr>
<td>ESA</td>
<td>Excited State Absorption</td>
</tr>
<tr>
<td>(4I_{15/2}, 4I_{13/2}, 4I_{11/2})</td>
<td>Energy levels in trivalent Erbium</td>
</tr>
<tr>
<td>LD</td>
<td>Laser Diode</td>
</tr>
<tr>
<td>SA</td>
<td>Saturable Absorber</td>
</tr>
<tr>
<td>SESAM</td>
<td>Semiconductor Saturable Absorber Mirror</td>
</tr>
<tr>
<td>SMF</td>
<td>Single-Mode Fiber</td>
</tr>
<tr>
<td>WDM</td>
<td>Wavelength Division Multiplexer</td>
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### Material and Chemical Abbreviations

<table>
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<th>Abbreviation</th>
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<tbody>
<tr>
<td>BP</td>
<td>Benzoyl Peroxide</td>
</tr>
<tr>
<td>CNT</td>
<td>Carbon Nanotube</td>
</tr>
<tr>
<td>DMF</td>
<td>Dimethylformamide</td>
</tr>
<tr>
<td>DPS</td>
<td>Diphenyl Sulfide</td>
</tr>
<tr>
<td>GMF</td>
<td>Glass Microfiber</td>
</tr>
<tr>
<td>MMA</td>
<td>Methyl-Methacrylate</td>
</tr>
<tr>
<td>PMMA</td>
<td>Poly-Methyl-Methacrylate</td>
</tr>
<tr>
<td>SDS</td>
<td>Sodium Dodecyl Sulfate</td>
</tr>
<tr>
<td>SF</td>
<td>Syringe Filter</td>
</tr>
<tr>
<td>SWCNT</td>
<td>Single-Walled Carbon Nanotube</td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>Aluminum Oxide</td>
</tr>
<tr>
<td>GeO(_2)</td>
<td>Germanium Oxide</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>Dihydrogen Monoxide</td>
</tr>
<tr>
<td>Er(^{3+})</td>
<td>Trivalent Erbium</td>
</tr>
<tr>
<td>Nd(^{3+})</td>
<td>Trivalent Neodymium</td>
</tr>
<tr>
<td>P(_2)O(_5)</td>
<td>Phosphorous Pentoxide</td>
</tr>
<tr>
<td>SiO(_2)</td>
<td>Silicon Dioxide</td>
</tr>
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Equipment and Machinery Abbreviations

BBS   Broadband Source
EDX   Energy-Dispersive X-ray
FPM   Fiber Power Meter
LDC   Laser Diode Controller
OSA   Optical Spectrum Analyzer
OTDR  Optical Time-Domain Reflectometer
SEM   Scanning Electron Microscope
WTLDS Wavelength-Tunable Laser Diode Source

LIST OF SYMBOLS

English symbols

ISU   Indiana State University
Tp    Thermally purified
1. INTRODUCTION

Pulsed fiber lasers find many uses ranging from fiber sensors such as range finders and gas or pressure sensors [1], optical time-domain reflectometry (OTDR) where high-power ultrafast laser pulses are required for accuracy in measurements [2], and numerous nonlinear optical purposes like harmonic generation or pumping of an acousto-optically gain-switched solid state crystal laser [3]. The all-fiber construction has some advantages compared to other solid state pulsed lasers. For example, all-fiber construction provides inherent robustness and relative compactness. Also, keeping the light constrained to a waveguide with no open-air propagation or alignment considerations improves both the short and long term stability of the system while simultaneously eliminating many potential noise sources. These benefits allow high pulse energy and repetition rate while maintaining ultrashort temporal durations ranging from microseconds ($\mu$s) to femtoseconds (fs). The combination of high pulse energy with ultrashort duration results in large peak powers, leading to uses in materials processing and the medical industry [4]. The incorporation of carbon nanotubes in the saturable absorbing device has advantages of its own compared to the common alternatives for creating saturable absorbers (SAs).

In large part, the SAs used for pulsed operation of fiber lasers are semiconducting saturable absorber mirrors (SESAMs), and they come with a high price tag and complex fabrication process. Additionally, the interaction of the laser light with the SESAM is limited to reflection only. Carbon nanotubes are well tailored for use as a nonlinear optical absorption material owing to their rapid saturation recovery time of ~1 picosecond (ps) or less, substantial optical damage threshold, and long-term physical and chemical reliability. There is a wide range of fabrication options for carbon nanotube (CNT) based SAs that are mostly cheaper, faster, and experimentally less complex than
that of SESAMs; furthermore, the various methods of incorporating these devices into the fiber laser cavity allows for various CNT-light interaction schemes, which in turn increases laser cavity design flexibility [5].

The organization of the thesis following this point is as follows. Chapter 2 provides a background and theoretical explanation of ring-cavity, erbium-doped fiber lasers (EDFLs) with a brief mathematical analysis. Chapter 3 contains a chronological progression of experiments and corresponding results which describe my process for the construction and continuous-wave (CW) operation of a ring-cavity EDFL. Some CW operational specifics are included in the last section of Chapter 3. Chapter 4 describes all the work performed with CNTs which eventually led to creation of CNT-based SAs, including characterization and purification of base CNT material. Chapter 5 begins with a theoretical explanation of Q-switching similar in style to Chapter 2, and then discusses the specific CNT-SA devices that successfully Q-switched the cavity and the corresponding laser output data such as the pulse train and optical spectrum. Chapter 6 summarizes the main results and overall success of the research. Finally, Chapter 7 outlines potential avenues of research for future students to undertake for the purpose of improving the Q-switched ring-cavity EDFL system developed during this research.
2. THEORY OF RING-CAVITY ERBIUM-DOPED FIBER LASERS

2.1 Erbium-Doped Fibers as Gain Media

Rare-earth doped fibers began being used as light amplifiers around the early 1960’s when Snitzer et al. made and tested glass fibers with trivalent neodymium (Nd$^{3+}$) as the dopant [6-8]. Here it was realized these wave guiding structures have the potential for huge advantages with respect to power densities since the light is confined to a small core region. As improvements in the fabrication of glass fibers are made, such as reducing the attenuation per unit distance, locating the minimum loss windows of silica glass at ~1.3 and ~1.5 µm, and the creation of single-mode fibers, other researchers capitalized on the earlier work of Snitzer et al. Namely, Payne et al. [9] first reported the potential for trivalent erbium (Er$^{3+}$) as a dopant for light amplification in silica fibers in 1987 [8]. Since then, many difficulties related to the fabrication of these erbium-doped silica fibers have been overcome. Two of the most noteworthy issues are the solubility and distribution of the rare-earth ions inside the silica fiber core. It has been found that incorporating compounds such as Si-O$, P_2$O$_5$, Al$_2$O$_3$, and GeO$_2$ into the silica glass core improves the solubility of Er$^{3+}$ in the silica, thus leading to higher weight percentages with less deleterious clustering of the ions [8-10]. Today, erbium-doped fibers play a large role in both the optical communications industry as power amplifiers as well as the fiber laser industry in general as gain sources for high-power continuous-wave fiber lasers and lower-power pulsed fiber lasers [11].

2.1.1 Pumping as a 3-Level System

The atomic energy band structure of erbium, more specifically the energy levels relevant for optical amplification using the erbium ion, Er$^{3+}$, is shown in Figure 2.1. In Figure 2.1, pump
photons are centered strictly at 980 nm, signal photons are centered at 1550 nm, and only the basic transitions of interest for this thesis are shown. Transitions not shown include absorption of pump photon at 1480 nm, excited state absorption (ESA), and multi-photon absorption; the latter two of these occur naturally and are a source of noise in the laser cavity, but these effects are not studied here. Also not shown in detail in Figure 2.1 is the variation of energy difference between the atomic energy levels. This energy variation, which is caused by atomic vibrations and is known as Stark Splitting, is responsible for the bandwidth of radiation around the center wavelength for both the pump and signal photons.

Section A to the far left represents the absorption of a pump photon of around 980 nm wavelength, which will promote an electron from the $^4I_{15/2}$ state to the $^4I_{11/2}$ state. From this level, the electron rapidly decays to the $^4I_{13/2}$ state in a few µs ($10^{-6}$ seconds) due to a multi-phonon transition; section E of Figure 2.1. This is a non-radiative transition and the energy lost by the electron is emitted as

Figure 2.1: Atomic energy band structure for the Er$^{3+}$ ion showing the three-level pumping scenario with possible transitions for the electrons. The signal photons for this energy transition are centered around 1550 nm.
thermal energy. The lifetime of the $^4I_{13/2}$ state is about 8-10 ms, which is three orders of magnitude longer than the lifetime of the $^4I_{11/2}$ state, meaning electrons being promoted to the $^4I_{11/2}$ state by 980 nm pumping will effectively collect in the $^4I_{13/2}$ state and allow a population inversion to occur [12-14]. A population inversion is the situation in which more of the Er$^{3+}$ ions contained within the erbium-doped fiber (EDF) are in an exited state than in the ground state, meaning there are more electrons in the upper levels of all the Er$^{3+}$ ions than there are in the ground level. A population inversion is a condition that is necessary for there to be any gain in the signal radiation; therefore, it is also necessary for lasing to occur. If we call the $^4I_{15/2}$ state level 0, the $^4I_{13/2}$ state level 1, and the $^4I_{11/2}$ state level 2, then it is easy to see why this is called a 3-level system. The absorption of a pump photon promotes an electron from level 0 to level 2, from which it almost immediately decays to level 1. The transition from level 1 to level 0 is the one of interest for optical gain in the C-band. Since the lifetime of level 1 is greater than 1000 times longer than the lifetime of level 2, photons can be placed into level 1 faster than they are removed by passing them through level 2, assuming there is enough pump photon flux. Thus, three levels are involved in the process of populating the level of interest.

Pumping with 980 nm light is not the only option with EDFs. One can also promote electrons from the $^4I_{15/2}$ state directly to the $^4I_{13/2}$ state using 1480 nm light, this transition is shown in Figure 2.1 section B, which also shows that the reabsorption of a signal photon will cause the same electron transition. Trivalent erbium ions have absorption peaks in other parts of the electromagnetic spectrum as well, including 380 nm and 520 nm. These bands absorb much more strongly than the 980 nm and 1480 nm bands albeit are rarely used due mainly to lack of high power laser diodes emitting in those wavelengths. There is also a small absorption peak at 800 nm, in which high power LDs are available, but this pump band is less attractive due to a phenomenon
called excited state absorption. Excited state absorption is the tendency for rare earth ions that are already in an excited state to absorb another photon, promoting the excited electron to an even higher energy level. This electron can then decay in a number of non-radiative or radiative ways, depending on the energy band structure of the excited rare earth ion. If its decay is entirely non-radiative, two pump photons are lost and no unwanted photons are created. However, in many cases its decay is at least partially radiative, emitting a photon most likely outside the signal bandwidth. In either case, the efficiency of the EDF is reduced in terms of achievable optical gain by reducing the ratio of emitted signal photons to absorbed pump photons, and in the radiative emission case, the noise is increased by creating more photons outside the signal bandwidth. Owing to the specific energy band structure of trivalent erbium, ESA does not occur for pump bands of 980 and 1480 nm. Taking into account the absence of ESA and the availability of high-power LDs in both the 980 and 1480 nm pump bands, these are the wavelengths of choice for most commercial devices employing EDFs for optical gain. [14-15]

2.1.2 Pumping Schemes: Unidirectional versus Bidirectional

Unidirectional pumping is the case in which pump radiation is only launched into one end of the EDF. As stated previously, when 980 nm pump radiation is launched into one end of the EDF, it begins to be absorbed by the Er\(^{3+}\) ions, putting them into an excited state. As this continues to happen, a population inversion can occur; however, the inversion is not constant along the length of the EDF. At the beginning of the EDF, where the pump light is coupled in, there are a set number of pump photons per unit volume inside the fiber. This number steadily decreases as the photons are absorbed by the Er\(^{3+}\) ions along the way, meaning the amount of pump light available at the end of the EDF is much less than at the beginning of the EDF. This means the population inversion
is not constant along the length of the EDF, thus, the gain of the EDF is not constant along its length either. In some circumstances, this could lead to issues in laser performance. In fact, if the length of the EDF is not optimized with the amount of available pump radiation, then it is possible to have some of the signal radiation being re-absorbed by the EDF instead of causing stimulated emission of more signal photons. A diagram of a unidirectional pumping scheme for an erbium-doped fiber amplifier is shown in Figure 2.2; WDM stands for wavelength division multiplexer and LD stands for laser diode.

![Diagram of unidirectional pumping scheme for an EDFA](image)

*Figure 2.2: Diagram of unidirectional pumping scheme for an EDFA.*

Bidirectional pumping is the case in which pump radiation is launched into both ends of the EDF. In this scenario, two WDMs are needed, one on either end of the EDF. A diagram of this can be seen in Figure 2.3. With the bidirectional pumping scheme, the amount of pump radiation available to be absorbed per unit volume inside the fiber is much more constant than it is for the unidirectional pumping scheme. Assuming lasers with the same output power are being used at the
pump sources, then approximately the same amount of pump radiation is available at either end of the EDF, with the intensity decreasing in the direction of the center of the EDF from either end. Again, optimization of the length of the EDF with the available pump power is necessary to optimize the gain of the cavity. However, bidirectional pumping does provide a more uniform population inversion along the length of the EDF.

![Diagram of bidirectional pumping scheme for an EDFA.](image)

2.1.3 Gain Characteristics

As stated previously, to achieve optical gain with an EDF, there must be a population inversion among the trivalent erbium ions inside the fiber. This is accomplished by pumping the EDF in one or more of the Er$^{3+}$ absorption bands with a sufficient amount of optical power. Once a population inversion is achieved, a single photon in the signal band can stimulate a cascade of emission whereby many more photons in the signal band are created. If more light in the signal band exits the erbium fiber than was introduced into it, then gain has been achieved.
2.2 Oscillation Condition for a Fiber Laser

As in any laser system, certain oscillation conditions must be met in order for the light amplification to continue and lasing to occur. As the pump radiation is absorbed along the length of the EDF, spontaneous emission in the signal band begins to happen, which then causes stimulated emission in the signal band. The creation of coherent signal photons by the stimulated emission process increases the amount of light in the signal band and is referred to as gain. Similarly, the reduction of the amount of coherent light in the signal band through processes such as absorption, scattering, etc., is referred to as loss. The general condition that must be satisfied for lasing to occur is that the gain be higher than the loss. As mentioned previously, a population inversion of the Er\(^{3+}\) ions is necessary for there to be any amount of gain.

2.2.1 Mathematical Analysis

The following is a simple mathematical analysis of the oscillation conditions for a fiber laser. Let us first consider the case for the un-pumped fiber laser. Without the pump radiation, population inversion is not possible, and the majority of the Er\(^{3+}\) ions are in the ground state. Since the Er\(^{3+}\) ions are not excited, no gain via spontaneous or stimulated emission will take place, only loss via absorption and scattering. Begin by defining \(I\) as the intensity of light inside the fiber, and \(\alpha\) the loss per centimeter at the signal wavelength. Then, the light intensity will decrease along the length of the fiber according to

\[ I = I_0 e^{-\alpha x} \]  \hspace{1cm} (2.1)

where \(x\) is the distance along the fiber, and \(I_0\) is the light intensity at \(x = 0\). So, for the un-pumped fiber, the intensity of light launched into one end will decay exponentially as it travels to the other end. Now, let us assume the EDF is pumped and a population inversion is achieved. As with the
loss, we can define the gain per centimeter generated by spontaneous and stimulated emission by \( \beta \). The net change in signal light per centimeter can then be found by taking the difference \( \beta - \alpha \).

It follows that for the pumped case, the light intensity in the fiber, defined by \( I_p \), is given by

\[
I_p = I_0 e^{(\beta - \alpha)x}.
\]  
\[\text{(2.2)}\]

Using a singular value for \( x \) makes the assumption that the pumped section of the fiber laser is the same length as the entire fiber laser. This is not necessarily true, and so leads to the creation of two new variables, \( l_t \) and \( l_p \), representing the total and pumped lengths, respectively. For simplification, let us assume that \( \beta \) is constant throughout the length \( l_p \) and that \( \alpha \) remains unsaturated. This leads to changes in the above equation for \( I_p \); the updated equation is

\[
I_p = I_0 e^{\beta l_p - \alpha l_t}.
\]  
\[\text{(2.3)}\]

The net gain can now be calculated as the ratio of \( I_p \) to \( I_0 \), generating the equation

\[
G = I_p / I_0 = e^{\beta l_p - \alpha l_t}.
\]  
\[\text{(2.4)}\]

Actually measuring this value of gain is complicated because measuring \( I_0 \), the intensity of light coupled into the gain fiber, is itself difficult. It is much simpler to measure the intensity of light output by the fiber laser. This way, the two signals being compared would be the intensity of light exiting the un-pumped fiber, \( I_u \), to the intensity of light exiting the pumped fiber, \( I_p \). The equation for the un-pumped case is
\[ I_u = I_0 e^{-\alpha l} \]  
which gives

\[ g = \frac{l_p}{l_u} = e^{\beta l_p} \]

as the equation for the gross gain. The above equation describes the amount of light amplification that can be achieved by a single pass of signal light through the pumped fiber. For oscillations to happen and lasing to occur, there must be a feedback mechanism in the cavity. The specifics of the feedback mechanism will be described in the next section. [7]

### 2.2.2 Feedback Mechanism

In a ring-cavity setup for an erbium fiber laser, the output of the EDF is connected back to the input of the EDF to make a continuous loop of fiber. A WDM is used to couple the pump radiation into the EDF from a separate source outside the cavity. Then, a feedback mechanism is connected between the output and input of the EDF. For a ring-cavity fiber laser, the device normally used as a feedback mechanism is a fiber coupler. The fiber coupler is a device that splits the light input to one arm into two separate arms that may or may not carry the same percentage of the input light. Some of the more common coupling ratios are 50/50, 70/30, 90/10, and 99/1. If, for example, a 50/50 coupler were used as the feedback mechanism in a fiber laser, 50% of the light exiting the amplification section of the fiber laser would be fed back into the beginning of the cavity, passing through the WDM and then back into the EDF, while the remaining 50% would be directed outside of the fiber loop as the output of the ring-cavity EDFL. A diagram of a ring-cavity EDFL can be seen in Figure 2.4; the isolator ensures unidirectional operation of the cavity.
Figure 2.4: Diagram of a ring-cavity EDFL using a 90/10 coupler as the feedback mechanism and a unidirectional pumping scheme.
3. CONSTRUCTION OF A CW RING-CAVITY ERBIUM-DOPED FIBER LASER

3.1 Characterization of the EDF

Before the ring-cavity EDFL can be built, the EDF being used must be characterized. Useful data to obtain about the EDF include the absorption and amplified spontaneous emission (ASE) spectra, the absorption and emission cross sections, and the gain at signal wavelength.

3.1.1 Signal Absorption and ASE Spectrum

The absorption and ASE spectrum of the EDF show the range of wavelengths in and near the C-band of the telecommunications windows which are readily absorbed and re-emitted by the Er$^{3+}$ ions in the fiber. The absorption spectrum is measured by incrementally passing a large range of wavelengths through the un-pumped EDF and comparing it to a reference to determine how much light per unit wavelength has been absorbed by the EDF. Amplified spontaneous emission is the accumulation of photons spread out over the entire emission band of one atomic transition in the Er$^{3+}$ ions due to spontaneously emitted photons causing the stimulated emission of more photons upon striking another excited Er$^{3+}$ ion. In other words, the ASE spectrum is the output of a pumped EDF when there is no feedback mechanism to allow lasing. Without a feedback mechanism, the oscillation conditions are not met, resulting in the spontaneous emission of incoherent photons across the entire emission band of the atomic transition of interest. Virtually all of these spontaneously emitted photons will see some amount of gain before exiting the EDF, leading to amplification of the spontaneous emission.
To measure the signal absorption spectra of the EDF, a wavelength-tunable laser diode source (WLTLDS) (photonetics Wavelength Tunable Laser Diode Source – SN 39203) is connected to an optical isolator which is then connected to the signal input to the WDM. The output of the un-pumped EDF is connected to another optical isolator which is then connected to a 90/10 coupler. The 90% arm is connected to the Agilent 86143B optical spectrum analyzer (OSA) while the 10% arm is connected to an ILX Lightwave fiber power meter (FPM) 8200 to monitor the optical power input to the EDF. The experimental setup can be seen in Figure 3.1. The 10% arm of the 90/10 coupler is connected to the FPM while the 90% arm is connected to the WDM; WTS stands for wavelength tunable source.

![Diagram of experimental setup for measuring the absorption spectrum of the EDF.](image)

*Figure 3.1: Diagram of experimental setup for measuring the absorption spectrum of the EDF.*

The output power of the WTLDS is set to 5 dBm and the wavelength is tuned from 1500 nm to 1580 nm in increments of 5 nm. The power exiting the 10% arm as well as the power exiting the isolator at the output of the EDF were recorded for each wavelength increment. The 10% arm power was used to calculate the power entering the EDF, and which is then compared to the power exiting the EDF to calculate the absorption at each wavelength interval. This is done using
MATLAB, and the results can be seen in Figure 3.2. The absorption is calculated by taking the difference of input power to output power.

![Absorption spectrum of Er110 fiber](image)

**Figure 3.2:** MATLAB plots of the data taken for the signal absorption spectrum.

To measure the ASE spectrum of the EDF, the 980 nm pump LD (Bookham Technology LC94C74) is used to excite the Er$^{3+}$ ions in the fiber. The pump LD is turned on and driven at maximum current of ~500 mA using the ILX Lightwave laser diode controller (LDC) 3900. The output of the pumped EDF is connected to the OSA and the resulting trace is saved. The experimental setup of this measurement is shown in Figure 3.3.
During the attempts to measure the ASE spectrum, unwanted oscillations began to occur that made the data taken unusable. Somewhere in the setup, multiple reflections were oscillating back and forth, passing through the EDF and experiencing gain. These oscillating reflections could have happened between the two fusion splices on either end of the EDF, between two fiber connector/physical contact (FC/PC) end connectors, between one fusion splice and one end connector, between the signal input to the WDM and its end connector, at the fiber/air/plastic protective cap interface at the end connector to the WDM signal input, or some combination of those. These deleterious reflections caused a very noisy peak to emerge from the ASE spectrum where there should only have been a rounded hilltop. The reflections would not plague the data for all pump LD powers; however, they normally began to emerge at a drive current of 300 mA and above. The trace data is imported to MATLAB to be plotted, and the results can be seen in Figure 3.4. The noisy peaks around 1530 nm are the result of these oscillating reflections.
Through trial and error, it was discovered that the reflections were most likely stemming from the interface between the end connector of the signal input to the WDM and the air immediately surrounding it. A solution to this problem is found by connecting an optical isolator to the signal input end of the WDM with its isolation direction oriented toward the EDF. An optical isolator is also connected to the output of the EDF with its isolation direction oriented away from the EDF. The experimental setup for this can be seen in Figure 3.5.
The presence of the isolator changed the interface at the signal input end of the WDM from a fiber/air interface to a fiber/fiber interface. Another fiber/air interface was created at the end of the isolator not connected to the WDM signal input; however, the amount of light reaching that interface was severely reduced by the isolator facing the opposite direction. This reduction in the power of the light reaching the fiber/air interface was sufficient to completely remove the noisy peaks in the ASE spectrum caused by oscillating reflections. The results of this experiment can be seen in Figure 3.6.
Figure 3.6: ASE spectrum of the EDF after isolators were used to stop the unwanted oscillations.

3.1.2 Calculating Absorption and Emission Cross Sections

The absorption and emission cross sections of the EDF are frequency-dependent effective areas of potential interaction describing interaction probabilities with photons travelling through the fiber. They can be used to calculate the probability of atomic transitions caused by optical interactions with the erbium ions in the EDF. There are numerous ways of measuring and calculating the cross sections. The method used here is the Fuchtbauer-Ladenburg equation. [16]

$$
\sigma_{em}(\lambda) = \frac{\lambda^5}{8\pi^2 n^2 \tau_{rad}} \int I(\lambda) d\lambda
$$

(3.1)
The subscript ‘em’ on the left hand side of the equation refers to emission cross section, the \( \lambda_p \) refers to the peak wavelength of the emission spectrum, and the \( \tau_{rad} \) refers to the radiative lifetime of the atomic transition of interest. On the far right of the equation, the wavelength-dependent intensity spectrum divided by its integral can be replaced by the normalized ASE spectrum of the EDF divided by the effective emission bandwidth. Making these substitutions results in the new equation.

\[
\sigma_{em}(\lambda) = \frac{\lambda_p^4}{8\pi c n^2 \tau_{rad} \Delta\lambda_{eff}} \frac{ASE(\lambda)}{ASE(\lambda)_{norm}}
\]

(3.2)

This equation is used to calculate the emission cross section of the EDF after the ASE spectrum is measured. The values of \( \lambda_p \) and \( \Delta\lambda_{eff} \) are taken from the plot of the ASE spectrum using MATLAB. This equation can be used for calculating the signal absorption cross section as well by replacing the normalized ASE spectrum with the normalized absorption spectrum, generating equation 3.3.

\[
\sigma_{abs}(\lambda) = \frac{\lambda_p^4}{8\pi c n^2 \tau_{rad} \Delta\lambda_{eff}} \frac{Abs(\lambda)}{Abs(\lambda)_{norm}}
\]

(3.3)

The absorption spectrum used in the calculation of the absorption cross section is simply the magnitude of absorption in dB per unit wavelength. Normalization of the absorption spectrum, as well as the emission spectrum, for the cross section calculations removes the units associated with that spectrum. It then follows that the final units for the cross sections are \([m^2]\). The calculations are done using MATLAB, and the results can be seen in Figure 3.7.
3.1.3 Measuring EDF Gain

The gain of the EDF is one of the most important parameters to characterize, it will be the threshold value determining how much cavity loss can be withstood and still achieve lasing. The single pass gain of the amplifier is determined by measuring the signal power input to and output from the fully pumped EDF and taking the difference of the two values. With the EDF fully pumped by the 980 nm pump LD, a small amount of signal radiation input to one end will cause stimulated emission as it travels through the length of the fiber. This stimulated emission will then cause further stimulated emission in a cascading effect along the fiber that will result in more signal photons exiting the EDF than were input to it. The amount of optical power exiting the EDF at the signal wavelength is the absolute signal gain.
in either decibels or watts. Taking this value and dividing it by the length of the amplifying fiber will give the gain parameter, in either decibels per meter (dB/m) or Watts per meter (W/m). The gain profile of the EDF is measured only at the peak emission wavelength of the emission cross section. To do this, the WTLDS is connected to an optical isolator followed by a 90/10 coupler. The 10% arm of the 90/10 coupler is connected to a FPM for constant monitoring of the signal power that is input to the EDF. The 90% arm is connected to the signal input arm of the WDM. With the EDF fully pumped by the 980 nm pump LD, signal light is input to the amplifier and both the 10% input optical power value as well as the optical power exiting isolator following the EDF are measured by a FPM and OSA, respectively. A diagram of this experimental setup is depicted in Figure 3.8. Gain plots are seen in Figures 3.9 and 3.10.

Figure 3.8: Experimental setup for measuring the gain profile of the EDF.
Figure 3.9: Output power versus input power through the fully pumped EDF. Signal wavelength is $1531 \pm 0.1$ nm.

Figure 3.10: Gain versus input power for the fully pumped EDF. Signal wavelength is $1531 \pm 0.1$ nm.
3.2 Ring Cavity Setup

The experimental setup for the ring-cavity erbium-doped fiber laser is quite simple and straightforward. The 980 nm pump laser diode output fiber is spliced into the 980 nm input arm of the 980/1550 nm WDM, the output of which is spliced directly into one end of the EDF. On the other end of the EDF, a small length of SMF has been spliced with a standard FC/PC connector on the end. Connected to this is an optical isolator with isolation direction oriented away from the EDF. After the isolator is a 90/10 coupler with the 90% arm feeding back into the cavity and the 10% arm being used for output. Following the 90% arm of the coupler is another optical isolator with isolation direction facing away from the coupler. This second isolator is connected on the opposite end to the 1550 nm arm of the 980/1550 nm WDM and so completes the fiber loop. A diagram of the ring cavity setup is depicted in Figure 3.11.

Figure 3.11: Setup of ring cavity for CW operation of ring-cavity EDFL.
3.3 CW Operation

With the cavity setup as shown in the previous section, operating the laser in the CW regime is as simple as pumping the EDF until threshold. The 10% arm of the 90/10 coupler is connected to an OSA to measure the spectrum and power of the laser output. With the pump laser diode controller turned on, the temperature is set to 25°C and the drive current is increased until threshold is reached and an output in the 1500-1600 nm range on the OSA is seen. The threshold drive current of the laser is 70 ± 1 mA, which corresponds to a pump laser diode output of 21 ± 0.5 mW. From there, the drive current can be increased up to a maximum of 500 mA, corresponding to 294.5 ± 0.5 mW of pump laser diode output power. The drive current to output power relationship for the 980 nm LD can be seen in the Figure 3.12.

![Graph of drive current vs optical output power for the 980 nm pump LD used in the ring-cavity erbium-doped fiber laser.](image-url)
Since the 980 nm pump LD is directly spliced into the 980 nm input arm of the WDM, which is in turn directly spliced to the EDF, the output power of the LD cannot be measured before it passes through the WDM and EDF. While the WDM has a negligible loss of $0.29 \pm 0.01$ dB for 980 nm light, the EDF certainly does not. So, measuring the output power exiting the EDF is not representative of the true output power of the 980 nm pump LD. In order to create this graph, a few numbers quoted in the specification sheet for the 980 nm pump LD that related drive current to output optical power were recorded. Then, MATLAB is used to interpolate the data points between those which I had taken from the specification sheet.

The output ASE spectrum of the pumped EDF ranges over 1520–1570 nm (see Figure 3.6), with a peak at $1530.3 \pm 0.1$ nm. However, when setup as a ring cavity, different components inside the cavity may limit the range of lasing possibilities. The WDM and both isolators employed in the ring cavity have operational bandwidths; these bandwidths could help select which region of the entire gain bandwidth of the EDF is allowed to lase. Under normal CW operation, with no added nonlinear materials, the cavity oscillates with a peak of $1558 \pm 1$ nm, and has an average power output of $4.5 \pm 0.5$ dBm.
4. CARBON NANOTUBE INVESTIGATION AND EXPERIMENTATION

The synthesis, application, and overall scientific understanding of single-walled carbon nanotubes has greatly expanded in the past 25 years since their first reported discovery by Sumio Iijima and others in the early 1990s [17-19].

A detailed history will not be presented here, but rather the work done by myself using single-walled carbon nanotubes (SWCNTs) purchased from U.S. Research Nanomaterials Inc. Among this work includes characterization of purchased SWCNTs, purification of the SWCNTs, dispersion of SWCNTs in to various organic solvents and H₂O, attempts to create SWCNT-polymer nanocomposites, and, finally using the SWCNTs to create saturable absorbers for insertion into the ring-cavity erbium-doped fiber laser.

4.1 Characterization Methods and Attempts

4.1.1 Scanning Electron Microscope (SEM) Imaging of SWCNTs

The first characterization method tried is to view the as-bought SWCNTs using a SEM. The purpose of this, initially, is to find out if the SWCNT soot purchased from U.S. Research Nanomaterials Inc. is actually >90% SWCNTs. Following the preparation protocols laid out in [20], I prepared a sample for viewing in the SEM. First the dry method is tried, then later the wet method is tried using multiple solvents for dispersion. Explanation of the production process of these SWCNT-organic solvent dispersions will be in a later section of this chapter. The specific SEM used is a Hitachi S-3000N, a picture of this SEM is shown in the Figure 4.1.
A high-quality SEM that can produce focused images at a magnification of 50,000 – 100,000 X can provide one with a good idea of CNT diameter and bundle sizes. There are two primary methods for preparing CNTs to be imaged with a SEM, a dry preparation and a wet preparation method. For both methods, all work is done in a fume hood to prevent the inhalation of CNT material and/or organic solvent vapors. The following steps outline the dry preparation method for imaging CNTs with a SEM.

Figure 4.1: SEM used for all imaging of SWCNT samples.
Dry Preparation:

1. Take a clean SEM stub and the CNT material and place them in a fume hood.

2. Attach a piece of carbon tape to the top surface of the SEM stub.

3. Using a metal scoop, place a small amount of CNT material onto the carbon tape and press lightly so it sticks.

4. Remove any excess CNT material by gently tapping the stub against a hard surface or lightly spraying the coated carbon tape with a clean nitrogen jet.

5. Place the stub with coated carbon tape into a storage container to be transported to the SEM for imaging.

An image of the prepared SEM stubs can be seen in Figure 4.2.

Figure 4.2: SEM stubs prepared for imaging SWCNTs using the dry preparation method.
As for the wet preparation method, first a solution must be made of SWCNTs dispersed into either an organic solvent or H$_2$O. The following steps outline the wet preparation method for imaging CNTs with a SEM.

**Wet Preparation:**

1. Weigh out a few milligrams of CNT soot and add them to 10–20 mL of an organic solvent such as dimethylformamide. A concentration of 0.0025 – 0.0250 wt% CNTs should be fine.

2. Sonicate the solution until the CNTs are well dispersed.

3. Take a small piece of a clean Si wafer and place it in a fume hood.

4. Using a micropipette, place a few drops of the CNT solution onto the Si wafer piece and allow to air dry.

5. Attach the backside of the coated Si wafer piece to a SEM stub using carbon tape.

6. Place the stub with the coated Si wafer piece into the SEM for imaging.
An image of the sample prepared for imaging using the wet preparation method can be seen in Figure 4.3.

Figure 4.3: Image of SWCNTs + dichloromethane dried on a Si wafer piece for imaging in a SEM.

The initial attempts at imaging the nanotubes are unsuccessful, mostly due to the SEM being unable to focus at a magnification high enough to see anything other than large clumps of material.
Images taken at low magnification for both the dry and wet preparation methods can be seen in Figures 4.4 and 4.5.

**Figure 4.4:** SWCNT soot on carbon tape imaged by SEM. The dry preparation method is used for this sample.

**Figure 4.5:** Solution of SWCNTs + isopropanol dried onto Si wafer. The wet preparation method is used for this sample.

Images taken at higher magnifications are not provided because they show no additional or different structures as the low magnification images. As can be seen in the above images, the only visible structures associated with the SWCNTs are large clumps of material. The magnification is far too low to be able to see any SWCNTs individually, if any are even present in that form. With
an average nanotube diameter of 1.1 nm, these bundles of material would easily contain thousands
to tens of thousands of nanotubes, as well as any impurities in the sample, whether inherent in the
purchased SWCNT material or introduced through the preparation methods.

After many trials, multiple solvents used, and multiple purification methods attempted,
much better images are taken that show a mesh-like network of material. The magnification is still
much too low to expect to see nanotube ropes or small bundles. The exact preparation method for
the sample imaged will be explained in detail in a later section of this chapter. The wet preparation
method is used with a solution of thermally purified SWCNTs dispersed into dimethylformamide
that is filtered post-sonication using a glass microfiber syringe filter with 0.45 µm retaining
diameter. The images of what should be the nanotube material are verified by energy-dispersive x-
ray (EDX) analysis, with the EDX spectrum showing a high carbon peak with a slight silicon
background. The presence of silicon is due to the use of a silicon wafer as the substrate on which
the SWCNTs were deposited. The EDX spectrum is provided along with the highest quality SEM
image obtained in Figures 4.6 and 4.7.
Figure 4.6: SEM images taken of prepared sample of SWCNTs using the most pristine solution I created to date. The wet preparation method is used for this sample.

Figure 4.7: EDX spectrum taken of same sample of SWCNTs as imaged above. The high carbon peak verifies that the SEM is focused on nanotube material.
4.1.2 Raman Spectroscopy of SWCNTs

Raman spectroscopy proved to be an indispensable tool used to investigate the SWCNTs bought from U.S. Research Nanomaterials Inc. as well as any dispersions created with the SWCNTs. The Raman microscope I used is a Kaiser Optical Systems Inc. Model RXN1-785(CUSTOM), a picture of this microscope is provided in the figure below. The Raman characterization is fairly simple and straightforward, and provided easy-to-interpret results that allowed me to determine properties such as relative amounts of amorphous carbons present in my samples as well as the presence of SWCNTs themselves. The paper “Raman spectroscopy of carbon nanotubes” was very helpful in this analysis [21].

Figure 4.8: Raman microscope used for all Raman analysis.
The first sample of SWCNTs that is analyzed using Raman spectroscopy is the SWCNT soot bought from U.S. Research Nanomaterials Inc. A small amount of this soot is scooped out of the bag and placed onto a glass microscope slide. The scoop is then used to lightly pat down the pile of soot so as to create a decently flat plateau of nanotube soot as opposed to the rough, mountain-like pile that is initially placed onto the slide. The slide is placed into the Raman microscope and aligned in the x-y plane so the laser is incident onto the nanotube soot. Then, the laser is turned on with a 1-second exposure time and the z-plane of the sample is swept up and down until the sample of nanotube soot is in maximum focus. Laser power and exposure time is varied to find the best-looking Raman spectrum. Once the optimum settings are achieved, the number of accumulations is increased so the final result is a smooth average of many measurements. In the figure below, the Raman spectra of two different brands of SWCNT soot are compared to that of just amorphous carbon powder. The SWCNTs from the company NanoLab are found in the lab with the Raman microscope and it was decided a good idea to compare them to the ones that had been purchased from U.S. Research Nanomaterials Inc. As can be seen in Figure 4.9, the two brands of SWCNT soot compare quite nicely, with the main difference being the central peak of the NanoLab SWCNTs being slightly higher than that of the U.S. Research Nanomaterials Inc. SWCNTs. The three peaks of interest can be seen by the data cursors at 1306 cm\(^{-1}\), 1580 cm\(^{-1}\), and 2583 cm\(^{-1}\), which correspond to the D, G, and G′ peaks, respectively. These three peaks represent the presence of carbon nanotubes in the sample [21]. It is worth noticing that the amorphous carbon powder has none of these peaks, only a slight uptick at the D and G peak areas, and no change at the G′ peak area. Another important aspect of this figure is the upward sloping trend at the right end of the graph. Past 2000 cm\(^{-1}\) all three spectra rise sharply, showing that there is a large amount of amorphous carbon present in both samples of the SWCNT soot.
Figure 4.9: MATLAB plot of the Raman spectra of two different brands of SWCNT soot and amorphous carbon powder. The data cursors mark the three peaks representative of SWCNTs.

The amorphous carbon impurities present in the SWCNT soot can be removed through a simple purification process. Following the procedure in [22], a dry oxidation technique is used to remove a large portion of the amorphous carbon impurities from my SWCNT soot. In my first attempt at removing the amorphous carbon impurities, I use the “Blue M Oven” in the MiNDS facility at Rose-Hulman. First, 105.1 ± 0.1 mg of SWCNT soot is weighed out and placed into a Pyrex vial. Then, the vial is placed without the lid into the oven at a temperature of 195 C. After 35 minutes, the oven reaches its maximum temperature of 253 C (claims a max of 260 C), and the
nanotubes are left in the oven for another 15 minutes. After the Pyrex vial has cooled down, the nanotubes are re-weighed and a loss of 6.3 ± 0.1 mg of SWCNT material is calculated. This corresponds to a loss of 6.0 ± 0.1 % mass of the initial SWCNT material placed into the oven. For the second, and all future trials of thermally purifying the SWCNT soot, a tube furnace in the MiNDS facility at Rose-Hulman is used. The tube furnace temperature is set to 300 °C, and a Pyrex vial containing 100.9 ± 0.1 mg of SWCNT soot is placed inside for a total time of 30 minutes. While inside the tube furnace, a clean flow of nitrogen is moving through the tube at a rate of 0.5 liters per minute. After removal from the furnace and re-weighing the Pyrex vial containing the nanotubes, a loss of 11.7 ± 0.1 mg, or 11.6 ± 0.1 %, of SWCNT material is calculated. Raman spectra are taken of both samples that were thermally purified and compared to that of unpurified, as-bought SWCNT soot from U.S. Research Nanomaterials Inc. The Raman spectra of these samples can be seen in Figure 4.10.
Figure 4.10: Raman spectra of SWCNTs after dry oxidation is performed to remove amorphous carbon impurities. (top) Dry oxidation at 253 C for 15 minutes. (bottom) Dry oxidation at 300 C for 30 minutes.
It can be seen in Figure 4.10 that the upward sloping trend past 2000 cm\(^{-1}\) is no longer present. This shows that the thermal purification process, called dry oxidation, is successful in removing a significant amount of amorphous carbon impurities from the SWCNT soot purchased from U.S. Research Nanomaterials Inc. Another point to notice is the prominence of the central peak at 1583 cm\(^{-1}\) for the SWCNTs that were thermally purified at 300 C compared to those purified at only 253 C. From the above figures, it can be conclusively stated that the dry oxidation of SWCNT soot at 300 C removes a large portion of the amorphous carbon impurities and results in a significantly higher quality SWCNT soot.

4.2 Dispersions of SWCNTs into Various Organic Solvents and H\(_2\)O

A crucial step in the process of both the characterization of and uses for SWCNTs is the ability to disperse them into liquids, namely, organic solvents or H\(_2\)O. These dispersions of SWCNTs are aimed to be very high quality, containing little to no SWCNT bundles and very few other impurities, such as amorphous carbons, fullerenes, or metal catalysts left over from the SWCNT production process [23-24]. In the soot form, individual SWCNTs adhere well to one another by van der Waals’ forces, forming large aggregates or clumps of SWCNT material. For one to effectively characterize SWCNTs, these naturally forming bundles must be broken up to minimal sizes, with a good majority of tubes being individualized. Without breaking up the SWCNT bundles, many interesting and exploitable properties of the nanotubes are effectively lost, one example is their incredible aspect ratio. The length to diameter aspect ratio of SWCNTs can range from 100’s to 10,000 or more, with the larger aspect ratios giving rise to some of the more intriguing and advantageous properties. It follows that, the more nanotubes you aggregate in one spot, bound to each other through van der Waals’ forces, the farther you stray from having actual SWCNTs, and the closer you get to having rather expensive amorphous carbon. For these reasons,
the creation of pristine solutions of nanotubes dispersed into either organic solvents or H\textsubscript{2}O is vital should they be used for further study or the creation of SWCNT devices such as SWCNT-polymer composites or nonlinear optical saturable absorbers [24-26].

Solutions are made of SWCNTs in three different organic solvents: dichloromethane, isopropanol, and dimethylformamide (DMF). Some attempts are also made at dispersing SWCNTs into H\textsubscript{2}O. For a few solutions the surfactant sodium dodecyl sulfate (SDS) is used as an additive to aid in the disaggregation of nanotube bundles. Specifically, SDS is added to solutions of SWCNT + DMF and SWCNT + H\textsubscript{2}O. Most of these solutions are made before access to a tip sonicator is available, so they are dispersed using a bath sonicator instead. A picture of the bath sonicator used can be seen in Figure 4.11.

![Figure 4.11: Crest brand bath sonicator used initially to disperse SWCNTs into organic solvents.](image-url)
The sonication process is excellent for dispersing nanotubes into a solution due to the cavitation effect. A sonicator produces ultrasonic waves that when passed through a liquid sample cause the formation of tiny voids where there is no liquid. These voids are extremely unstable and almost immediately collapse, producing a powerful shockwave when they do so. The shockwaves produced by the collapsing voids produce very high local temperatures and pressures, and cause the nearby nanotube bundles to break apart. Bath sonicators deliver a much lower power to the sample solution than do tip sonicators, meaning less cavitation. Due to this, the processing times with a bath sonicator are significantly longer than with tip sonicators. Also, even at longer processing times, the bath sonicator does not disperse the SWCNTs nearly as well as a tip sonicator.

For most solutions made using a bath sonicator, nanomaterials begin precipitating out within 10-20 minutes of stopping the sonication, whereas the solutions made using a tip sonicator stay stable without precipitation for days to weeks. The processing time in the bath sonicator is never shorter than 90 minutes but is usually run for 3+ hours, while the processing time with the tip sonicator is only 30 minutes at most. The pictures in Figure 4.12 show a time progression of nanomaterials precipitating out of bath-sonicated solutions of SWCNTs plus organic solvent.
The concentration of SWCNTs in the samples above is $0.08 \pm 0.02$ wt%, which is fairly heavy. Future solutions are aimed more at the range of 0.0025 wt% up to 0.01 wt% SWCNTs. However, the precipitation rates are not significantly decreased by a reduction of SWCNT concentration nor
by an addition of sonication time, up to a maximum of 6 hours of sonication. After numerous repeated trials with multiple solvents and H₂O, with and without the addition of SDS, the conclusion is reached that a bath sonicator is simply insufficient for creating high-quality, homogenous dispersions of SWCNTs.

The tip sonicator accessed is located in the lab of Dr. H. Kathleen Dannelly (Science Building 295A) in the Biology Department at ISU. Specifically, it is a Fisher Scientific FB120 sonicator using the FB 4422 sonicating tip. A tip sonicator uses an electric waveform generator to produce an ultrasonic signal which it then uses to drive a piezoelectric transducer. The piezoelectric transducer transforms the electrical signal into mechanical vibrations that are amplified then transmitted down the length of the probe tip. The probe tip then oscillates back and forth inside the sample solution at ultrasonic frequencies, causing cavitation. The waveform generated by this specific model of sonicator has a set frequency of 20 kHz. The magnitude of the oscillation, or the distance the tip travels back and forth as it vibrates, can be controlled over a certain range using the amplitude settings.

For sample sizes of 15 mL or less, a probe tip size of 1/8 inch is used. The vial containing the solution to be processed is suspended by the neck using a ring stand and clamp. The solution vial is maneuvered under the probe tip and then raised up until the probe tip is submerged to 1/3 of the way to the bottom of the vial from the liquid/air interface. A beaker of ice is placed underneath the vial of solution so that most of the outer surface of the vial is contacted by the ice. This keeps the sample cool during sonication as the cavitation effect will raise the temperature of the solution significantly over time. Depending on how long the processing time is, some of the ice may need to be replaced before the solution is done being sonicated.
Once the setup is complete, the sonicator is then turned on, the amplitude and processing time is set to the desired value, and the solution is monitored while the sonication is ongoing. A diagram of the physical setup can be seen in Figure 4.13. The beaker shown is filled with ice, the solution vial is placed in the ice and clamped into place via the ring stand and a beaker clamp (not shown).

![Diagram of tip sonicator and basic setup for processing SWCNT plus organic solvent solutions.](image)

Even about 4 months after the initial dispersion, the tip sonicated solution of SWCNTs in DMF has a set amount of precipitate sitting at the bottom while the rest of the solution remains homogeneous; out of which no more is precipitate is falling. It is reasonable to say the materials which have precipitated out are mostly carbonaceous impurities and metal ions that are not dissolved into the organic solvent DMF, but this is not confirmed.
Later, this precipitate will be removed by filtration. The specifics of this filtration process will be explained in a later section of this chapter. A picture of the pristine solution of SWCNTs in DMF, post filtration, can be seen in Figure 4.14.

![Figure 4.14: Pristine solution of SWCNTs in DMF. The SWCNTs are thermally purified before being dispersed. Dispersion is done using a tip sonicator and precipitate is removed by filtration.](image)

As is done with most solutions of SWCNTs in organic solvent, a Raman spectrum of the solution is taken to verify the presence of SWCNT material. A Raman spectrum of the pure organic solvent used in each case is also taken so the peaks representing SWCNTs are distinguishable from the organic solvent background. These spectra can be seen in Figure 4.15.
Figure 4.15: (top) Raman spectrum of pristine solution of SWCNTs in DMF. (bottom) Raman spectra showing the peaks representing the presence of SWCNT materials in the solution as well as pure DMF.
4.3 Use of SWCNTs to Make Saturable Absorbers

This section explains the process by which one can start with unpurified SWCNT soot, create a pristine SWCNT-organic solvent solution, and how to use that solution to make a saturable absorber.

First, an amount of SWCNT soot is thermally purified via the dry oxidation technique described earlier in this chapter. From the thermally purified SWCNT soot, a small amount is weighed out for dispersion into an organic solvent. The target concentration aimed for is 0.0025 % to 0.01 % SWCNTs by mass. So, for 15mL of solution using DMF as the organic solvent, this corresponds to an amount of SWCNT soot of 0.36 to 1.44 mg. Since these amounts are very difficult to weigh out accurately due to the inherent error of the digital mass scale being used, a solution with 10 times the desired concentration is made and then diluted appropriately via the following process. The initial high-concentration solution is sonicated, a small volume of which is removed and added to a measured amount of pure DMF for dilution, and then the diluted solution is sonicated to ensure homogeneity. The dispersion process is best done with a tip sonicator, as mentioned previously. With the model of sonicator accessed at ISU, an amplitude setting of 40% and a sonication time of 30 minutes is repeatedly used. Once the solution is sonicated, it is left in a sealed Pyrex vial at room temperature for at least 3 days to allow any undispersed SWCNT bundles and remaining impurities to precipitate out. Then the solution is filtered using a glass microfiber syringe filter with 0.45 µm retaining diameter to remove all the visible precipitate as well as any nanotube bundles larger than 0.45 µm that have not yet precipitated. Post filtration, a highly homogeneous, temporally stable solution of SWCNTs in DMF remains. From this solution, a saturable absorber is easily created directly inside the laser cavity by coating the end facet of one of the fibers. In order to coat a fiber end facet with one of these nanotube solutions, a ring stand
and clamp is used to hold the fiber end facet stationary and oriented vertically toward the ceiling, then a single drop of solution is placed onto the end facet using a micropipette. Careful placement of the drop results in a semi-circular blob of liquid sitting on top of the end facet. Once in place, the drop of solution is allowed multiple hours to dry, usually two to four depending on the solvent. Precise observation of drying time for each distinct case is not done. Once one drop has dried, another is placed in the same way and allowed to dry. This process is repeated to build up multiple layers of SWCNTs onto the fiber end facet one drop at a time. As the number of layers increases, a light black shading begins to be visible on the fiber end facet showing that the SWCNTs diffuse out of the host solution and adhere onto the end facet as the solvent evaporates. Once the desired number of layers is reached, the fiber is reconnected into the ring-cavity and the laser turned on to test the effectiveness of the deposited SWCNTs as a saturable absorber. The specific process flow of this direct coating method with respect to each successful case is provided in Chapter 5.2 along with images of the progression of layer build-up.

Another way to use the SWCNTs as a saturable absorber is by making a polymer-nanotube composite material that is then inserted into the cavity. The SWCNT-polymer composite is not synthesized directly onto the fiber end facet as in the solution-coating case, but once it is made it is easily inserted into the cavity by placing a small piece of it inside one of the FC/PC fiber connectors. The SWCNT-polymer nanocomposite material is created from a solution of SWCNTs dispersed in diphenyl sulfide (DPS) which is then added to pure liquid MMA that is then polymerized to form a SWCNT PMMA composite material. The procedure outlined in [27] is closely followed for these experiments. The omission of specific details from the procedure in [27] make the replication of a SWCNT PMMA nanocomposite film a trial and error process with subsequent trials giving vastly varying end results. Of the ten or more attempts made, only one
produced a malleable film with a light black coloration evenly throughout, with other results including a yellowy fluid that never solidified, transparent crystalline chunks, and a black solid material too hard for manipulation and insertion into the ring cavity. The one successful trial is now explained in detail. First, a solution of SWCNTs dispersed into DPS at a concentration of 50 ppm SWCNTs is made. A measured amount of that solution is then added to 10 mL of MMA which is placed into the bath sonicator. While sonicating, 1.135 ± 0.001 g of benzoyl peroxide (BP) is added as a polymerization initiator for the MMA. The BP must be thermally activated before the polymerization reaction can take place, however, the sonication provides enough energy to dissolve the BP and begin the polymerization of the MMA at room temperature. The polymerization process aids in the dis-agglomeration of SWCNT bundles and the DPS acts as a solution stabilizer to help prevent the re-agglomeration of already broken up SWCNT bundles while the polymerization takes place [27]. After 3 ± 0.5 hours of sonication a solid but malleable polymer is formed. There are some areas where air is trapped but for the most part it looks fairly homogeneous and is a light black color. A picture of the SWCNT-PMMA film can be seen in Figure 4.16.
Figure 4.16: Pictures of successful creation of SWCNT-PMMA composite film. [Left]-view from above. [Right]-view from the side.
5. PULSING THE LASER CAVITY

5.1 Q-Switching Theory

The term Q-switching refers to one of two main methods used to operate lasers in the pulsed, rather than CW, regime, the other method being mode-locking. Q-switching creates a pulsed output by periodically varying the Q-factor of the laser cavity such that the energy output of the laser oscillates rapidly. The Q-factor, or quality factor, of a laser cavity is defined as the energy stored in the resonator divided by the energy lost per resonator cycle multiplied by 2*pi; shown in the following equation. [28-29]

\[ Q = 2\pi \times \frac{\text{energy stored in resonator}}{\text{energy lost per resonator cycle}} \]  

Thus, the higher the Q-factor the higher the potential energy output from the resonator. Typical Q-factor values are highly positive; however, not all of the stored energy gets transformed into coherent photons of the desired frequency during each resonator cycle, and of the percentage that does, a certain amount is lost before it can escape the cavity as useable light. Regardless, variation of the Q-factor results in variation of the energy output of the laser. Specifically in the case of Q-switching, the Q-factor is changed by changing the cavity losses, and thereby the energy output.

There are two types of Q-switching techniques, active Q-switching and passive Q-switching. An active Q-switch is a device inserted into the laser cavity that is controlled externally to modulate the cavity losses, such as an acousto-optic switch or fast shutter. A passive Q-switch is a device which modulates the cavity losses without external control, such as a saturable absorber. In both cases, the cavity losses are modulated such that the overall loss is varied between values greater than and less than the cavity gain. Assuming there is a pumped gain medium within a
resonator cavity, when the cavity loss is higher than the gain, lasing cannot occur and the laser is effectively ‘off’, then, when the loss is reduced to be less than the gain, the laser ‘turns on’, and light is produced. So, the Q-switch effectively acts as an ‘on/off’ switch for the laser cavity by modulating the cavity losses appropriately.

A step-by-step explanation of the pulse formation via Q-switching is as follows. Initially, the cavity is in a high-loss state, the total resonator loss is greater than the total resonator gain, and energy from the pump source accumulates in the gain medium. The maximum potential amount of stored energy is generally limited by spontaneous emission or available pump energy, however, the high-loss state allows more energy to be stored in the gain medium than is present during CW operation. Then, the cavity is switched to a low-loss state, causing the energy stored in the gain medium to be released. When the loss is suddenly dropped, spontaneous emission noise from the gain medium is allowed to amplify via multiple resonator round-trips. This amplification of the noise spike occurs very rapidly, quickly generating high intra-cavity powers which saturate the gain. Once gain saturation is reached, the intra-cavity power decreases as the remaining energy stored in the gain medium is extracted. If the loss remains in the low state, an equilibrium will be reached between the energy provided to the gain medium via pumping and the energy extracted from the gain medium via lasing, and the laser will once again operate in a continuous state. If, instead, the cavity is switched back to the high-loss state, energy stored in the gain medium is allowed to replenish to high levels, and the process can be repeated. In summary, the high-loss state allows more energy to be stored in the gain medium than during CW operation, the sudden drop to a low-loss state rapidly depletes the stored energy faster than the pump can replenish it, and this rapid depletion of stored energy generates a large spike in light output, or a pulse [30].
Figure 5.1 illustrates the general relationship between cavity gain, cavity loss, and output pulse formation over time for a passively Q-switched laser.

![Figure 5.1: Temporal relationship of gain and loss in the laser cavity and resultant pulse formation for a passively Q-switched laser. [30]](image)

Saturable absorbers are used for the passive modulation of cavity loss that is needed for pulse formation. The two qualities needed for a material to be a good saturable absorber is a large absorption cross section overlapping the laser wavelength and a bleaching effect under higher optical powers [31-32]. Saturable absorbers are generally easier to integrate into a laser cavity than any active means of Q-switching and require no controlling electronics. Many materials have been used for Q-switching operation in the past, including doped bulk crystals and semiconductor saturable-absorber mirrors (SESAMs) [33], optical dyes and crystals with color center defects [34], SWCNTs [35], and graphene [33-36]. Doped bulk crystals and crystals with color center defects require extra optics to focus the laser output into the crystal [33-34], SESAMs have limited
operating bandwidths [33], and optical dyes have poor lifetime and thermal stability [34], leaving SWCNTs and graphene as the two best candidates for saturable absorbers [33-36].

The following mathematical analysis provides a few of the equations used to describe the passively Q-switched laser. Equations 5.2 – 5.4 are coupled rate equations from which all other necessary terms may be derived. The rate equations here are similar to those of a laser operating in the CW regime, however, the effect of a saturable absorber being present in the cavity is included. The Equations 5.2 – 5.8 presented here, along with their explanations, are taken from the work of Degnan [37], which themselves are a modified version of the work of Szabo and Stein [32].

\[ \frac{d\Phi}{dt} = \left[ 2\sigma n l - 2\sigma_s n_s l_s - \left( \ln \left( \frac{1}{R} \right) + L \right) \right] \frac{\Phi}{t_r} \quad (5.2) \]

\[ \frac{dn}{dt} = -\gamma \sigma c \Phi n \quad (5.3) \]

\[ \frac{dn_s}{dt} = -\gamma_s \sigma_s c \Phi n_s \quad (5.4) \]

In Equations 5.2 – 5.4, $\Phi$ represents the photon density, $n$ represents the instantaneous population inversion density in the gain medium, $n_s$ represents the instantaneous population density of the saturable absorbing medium, $\sigma$ and $\sigma_s$ correspond to the gain medium stimulated emission cross section and the SA absorption cross section respectively, $l$ and $l_s$ are the lengths of the gain medium and absorption medium respectively, $R$ is the reflectivity of the output mirror, and $L$ is the non-useful optical loss [37]. The term $t_r$ is the round-trip time of light travelling in the resonator and is defined by the following equation,

\[ t_r = 2l'/c \quad (5.5) \]
where \( l' \) is the length of the optical cavity. Keep in mind that the mathematical analysis done in this paper assumed a linear cavity using bulk optical components instead of a ring-cavity using optical fibers. This difference will change a few things about the base rate equations. Firstly, rather than an output mirror, light exits the cavity via a fiber coupler with 10\% of the intra-cavity power escaping with each round trip. This corresponds to an output mirror with \( R \) being equal to 0.9. Secondly, the round-trip transit time will not have the factor of 2 in the numerator as in Equation 5.5. This is because in a ring-cavity one round trip distance is equal to a single multiple of the length of the whole loop. The intra-cavity light passes through the gain medium only once per round trip. So, in this specific case, the term \( t_r \) is defined by Equation 5.6,

\[
t_r = \frac{l'}{c}
\]

(5.6)

where, of course, \( l' \) and \( c \) have the same meaning as before. From Equations 5.2 – 5.4, ignoring the change to \( t_r \) which is for ring-cavity lasers. Many useful relationships can be derived. Only one example is mentioned here as the rest have more to do with calculating the pulse output energy and temporal width; work that is not done for this thesis. Measurements of pulse duration for recorded Q-switching cases are taken from the data directly, not calculated using specific laser parameters and corresponding equations. One of these two useful relationships is shown in Equation 5.7,

\[
n_s = n_{si} \left[ \frac{n}{n_i} \right]^\alpha
\]

(5.7)

where \( n_{si} \) is the initial density of the absorbing state of the SA, \( n_i \) is the population inversion density in the gain medium at the onset of Q-switching, and the term \( \alpha \) is defined as the following.

\[
\alpha = \frac{\nu_0 \sigma_s D_a}{\gamma \sigma D_s}
\]

(5.8)
5.2 Q-Switched Laser Output Results

Passive Q-switching of the ring-cavity erbium-doped fiber laser is successful with four distinct saturable absorbers. Three of the four utilize a direct coating method whereby the end facet of one of the fibers in the cavity is coated with multiple dried layers of a solution of SWCNTs dispersed into an organic solvent. The first and second cases of pulsed operation are seen with SWCNTs in isopropanol and the third case with SWCNTs in DMF. The fourth successful SA that produces Q-switched pulses is a SWCNT-PMMA composite film that is sandwiched between two fiber end facets by inserting it into one of the FC/PC connectors in the cavity.

5.2.1 Direct Coating of Fiber End Facet with SWCNTs in Organic Solvent Solution and Corresponding Q-Switching Results

The initial achievement of pulsed output from the laser cavity comes after coating the end facet of the 90% output arm of the 90/10 coupler with multiple layers of SWCNTs in isopropanol solution. A minimum of three layers is generally required to see any color change, however, one- and two-layer SAs are also tested for pulse formation. The maximum number of layers tested is ten. Coincidently, the two SAs which passively Q-switch the laser using the SWCNTs in isopropanol solution have 3 layers and 10 layers, respectively. Also tested are SAs with 4, 5, 6, 7, 8, and 9 layers with no pulse formation occurring. All SAs created from the SWCNTs in isopropanol solution are formed layer-by-layer by drying in air; the fiber end facet is left uncovered. If accidental contact with the end facet results in a loss or change of the SWCNT material on the surface, the end facet is wiped clean and the layer formation process is restarted. In each case, the deposition of SWCNT material on the end facet seems arbitrary with uneven
concentrations of black material spread over the whole top surface of the ferrule. The distribution of SWCNTs across the fiber end facet is far from homogeneous, and differs from trial to trial. Considering that a polarization controller nor any polarization maintaining fiber (PMF) is used in the laser cavity, the poor distribution of SWCNTs across the end facet leads to unpredictable and random interaction with the light passing through the SA with each round trip. This, in turn, produces rather unstable pulses with rapid variations in pulse energy and temporal duration. Occasionally, the Q-switching ceases entirely and the pump power has to be varied to regain pulsed operation.

Another factor which potentially leads to unstable Q-switching is the initial quality of the SWCNTs in isopropanol solution being used. Although the majority of large agglomerations that are visible with the naked eye are filtered out, this solution is made before access to a tip sonicator. So the overall quality of this dispersion is poor in comparison to future dispersions used in the other successful Q-switching cases. A larger average bundle size of the SWCNTs on the end facet produces a lower quality SA, resulting in lower quality pulses and instability in the laser cavity. Pictures of the SAs with various number of layers is shown in the Figure 5.2.
Figure 5.2: Pictures of SAs made by direct coating of fiber end facet with SWCNTs in isopropanol solution. From Left to Right, Top to Bottom, the number of layers of dried solution are 0, 2, 3, 4, 5, 6, 7, 8, and 10.

Pictures of 1 and 9 layers are not shown because 1 layer is indistinguishable from 2 layers with this quality of picture and adding the 9th-layer picture results in an awkwardly shaped figure without providing any additional useful information. It is rather easy to notice the uneven deposition of SWCNT material in the pictures above, fortunately, this issue is later solved when making SAs using a pristine solution of SWCNTs in DMF.
To measure the output pulse trains of the passively Q-switched ring-cavity erbium-doped fiber laser, the 10% arm of the 90/10 coupler is connected to a ThorLabs PDA 400 fast photodiode after passing through a JDS Uniphase HA9 variable optical attenuator, and the photodiode output is measured with an Agilent 86143B oscilloscope. The output pulses for both the 3-layer and the 10-layer SAs are shown in the Figure 5.3.

![Q-switching pulse trains for SWCNT SA deposited onto fiber end facet](image)

**Figure 5.3:** Oscilloscope traces of the output pulse trains when the laser is passively Q-switched with SA made by direct coating of fiber end facet using low quality solution of SWCNTs in isopropanol.

The pulse train formed by the 10-layer SA has a repetition rate of $25.36 \pm 0.53$ kHz and an average temporal pulse width of $17.45 \pm 0.11$ µs at half-maximum, while the pulse train formed by the 3-layer SA has a repetition rate of $37.77 \pm 0.33$ kHz and an average temporal pulse width of $2.74 \pm 0.14$ µs. Apart from the higher repetition rate and shorter temporal width of the pulses formed by
the 3-layer SA, they are significantly sharper and the mechanism by which they are formed behaves more like an on/off switch; whereas, the 10-layer SA formed pulses that are much more oscillatory in nature and smoothly transition from one to the next. Also, there is complete termination of light output from the cavity between the pulses of the 3-layer SA, which is not true for the 10-layer SA. The output optical spectrum for these pulses is not measured by an OSA, and therefore is not shown.

Another SA made by the direct coating method is successful in Q-switching the cavity; however, this SA is made with a solution of thermally purified SWCNTs (tp-SWCNTs) dispersed in DMF using a tip sonicator, and the solution is filtered post-sonication by a glass microfiber (GMF) syringe filter with a 0.45 µm retaining diameter. Again, individual drops of solution are placed onto the fiber end facet and allowed to dry, only this time a rubber dust cap is placed over the end facet so the drying drop of solution is not exposed to ambient light nor the impurities present in open air during the drying process. Instead of drying arbitrarily in uneven clumps across the entire top surface of the ferrule as occurred without the dust cap, the deposition of SWCNTs is confined to a small circular spot centered on the glass core and has a visually uniform distribution. The increased quality of the solution used in this case may also be a contributing factor to the improved deposition of SWCNTs; however, this is unverified. However unexpected, this is a much-desired improvement in the direct coating method of SA creation. Passive Q-switching is achieved with only a 2-layer deposition, and the Q-switching occurs over a much larger pump power range, but becomes unstable at very high pump powers. Figures 5.4 and 5.5 show the Q-switched output of the SA formed by direct coating method using a solution of tp-SWCNTs in DMF that is tip sonicated and GMF SF filtered.
Figure 5.4: Q-switching operation at pump LD drive current of 227 mA with SA made by direct coating of fiber end facet using pristine solution of purified SWCNTs in DMF. (Top) - Pulses seen with oscilloscope. (Bottom) – Optical spectrum.
Figure 5.5: Q-switching operation at pump LD drive current of 430 mA with SA made by direct coating of fiber end facet using pristine solution of tp-SWCNTs in DMF. (Top) - Pulses seen with oscilloscope. (Bottom) – Optical spectrum.
The pulses formed at a pump LD drive current of 227 mA, which are shown in the top of Figure 5.4, have a repetition rate of $25.13 \pm 0.63$ kHz and a temporal duration of $12.28 \pm 1.08$ µs. The optical spectrum of the Q-switched laser for the same pump LD drive current, seen in the bottom of Figure 5.4, has a peak of $1557.40 \pm 0.05$ nm and a FWHM of $0.37 \pm 0.02$ nm. Increasing the pump LD drive current to 430 mA only slightly increases the repetition rate of the output pulses to $26.46 \pm 0.13$ kHz, but it has a significant effect on the temporal width of the pulses, decreasing that value to $3.58 \pm 0.12$ µs. The most noticeable change, however, is seen in the output optical spectrum, shown in the bottom of Figure 5.5. With the increase in pump LD power, the optical spectrum changes from a single peak at $1557.40 \pm 0.05$ nm with a few side lobes to a dual peak at $1531.7 \pm 0.5$ nm and $1556.9 \pm 0.35$ nm, with FWHMs of $2.05 \pm 0.05$ nm and $1.25 \pm 0.05$ nm, respectively.

The dual-peak spectrum is plagued with severe noise, and data-point averaging is done using MATLAB to smooth out the noisy oscillations and allow accurate wavelength peaks and FWHMs to be found. Sometimes at higher pump powers pulses are lost completely; to regain the Q-switching operation the pump power has to be lowered and then slowly brought back to higher powers. Normally, this results in unstable pulses and spectral shifts from single to dual operating wavelength peaks. Perhaps due to very high intra-cavity powers, the SWCNT SA is being damaged over time which results in erratic and unpredictable pulse and spectral output changes. For the higher pump LD drive current of 430 mA, a noise spike in the $1556.9 \pm 0.35$ nm wavelength peak outputs a maximum power of $0.74 \pm 0.02$ dBm as read by the OSA used to take the data in the bottom of Figure 5.5. The light reaching the OSA for that measurement exits the laser cavity from the 10% arm of the 90/10 output coupler and then passes through a 3 dB splitter. Intra-cavity power...
is $9.54 \pm 0.01$ dB higher than the light exiting the 10% arm, and then adding another 3 dB for the subsequent 50/50 splitter gives an intra-cavity power of approximately $12.54 \pm 0.01$ dB higher than the power measured by the OSA. With a standard SMF core size of 9 µm, the maximum optical intensity passing through the SWCNT SA is close to $33.55 \pm 0.01$ kW/cm$^2$.

5.2.2 Inserting the Composite Film SA Between Two Fiber End Facets and Corresponding Q-Switching Results

As discussed in Chapter 4 Section 3, multiple attempts are made at creating a SWCNT-PMMA composite device, with only one trial resulting in a useable film. Images of the film used for SA testing are shown in Figure 4.16. From that flexible polymer nanotube-composite material, tiny cylindrical pieces are cut out and inserted into a FC/PC connector so it becomes sandwiched between two fiber end facets. As was done previously, to test each piece for Q-switching capability, the drive current for the pump LD is slowly increased while watching for changes in the oscilloscope reading. Sometimes the pieces produce pulses and sometimes they do not. It is difficult to insert them into the connector while maintaining an orientation perpendicular to the direction of travel of light in the cavity. Occasionally the pieces of SWCNT-PMMA polymer composite become angled and/or misshapen inside the connector, which causes erratic interaction with the light passing through. For at least one piece of SWCNT-PMMA polymer composite sandwiched between two fiber end facets, stable pulses are formed and both the pulses and spectrum are measured. The results are shown in the Figure 5.6.
Figure 5.6: Q-switching operation with SWCNT-PMMA composite film sandwiched between two fiber end facets. (Top) – Pulses seen with oscilloscope. (Bottom) – Optical spectrum.
The pulses in the upper section of Figure 5.6 are separated by 7.00 ± 0.05 µs each, giving a pulse repetition rate of 142.8 ± 1 kHz. The average pulse temporal width measured at half-maximum is 716 ± 7 ns. The specifics of the optical spectrum are actually provided in the inset of the bottom plot of Figure 5.6. The spectrum peak wavelength is 1531.30 ± 0.05 nm and the FWHM is 2.60 ± 0.05 nm. Overall, the pulses formed by the SWCNT-PMMA polymer composite film sandwiched between two fiber end facets are the most stable, have the highest repetition rate with the shortest temporal pulse width, and provide the widest optical spectrum with a single peak.
6. CONCLUSIONS AND FUTURE WORKS

6.1 Conclusions

A ring-cavity fiber laser was built using a highly-doped erbium fiber 44.5 ± 0.2 cm in length. The other components include two optical isolators to ensure unidirectional operation, a WDM for combining the 980 nm pump light from the pump LD with the 1550 nm signal light being produced from the pumped EDF, and a 90/10 coupler for the output. The ring-cavity EDFL operates as a CW laser with a pump threshold of 21 ± 0.5 mW, and outputs 4.5 ± 0.5 dBm of signal radiation at 1558 ± 1 nm with a full pump power of 294.5 ± 0.5 mW at 980 nm. The total cavity length equals 11.97 ± 0.05 m.

The work done with carbon nanotubes involves characterization, purification, solution dispersion, and SA construction using the SWCNT dispersions. Characterization is done using SEM imaging, EDX analysis, and a significant amount of Raman spectroscopy. These tools allowed me to get a much better understanding of the initial material I worked with and its overall base quality. Purification and solution dispersion techniques and attempts are performed simultaneously, and much progress was made in each endeavor. Throughout this process, Raman spectroscopy is by far the most powerful investigative tool as it is continuously used to provide quantifiable, visible evidence of the progression and success of my experiments with carbon nanotubes. By the end of this research, a step-by-step method was developed to take unpurified SWCNT soot, purify it, disperse it into an organic solvent, and then further purify that dispersion, resulting in a high-quality, homogeneous, long-lasting and stable solution of purified SWCNTs in organic solvent.
Manufacture of working SAs by use of the SWCNTs in organic solvent solutions is successful in two distinct ways; one by deposition of SWCNTs onto fiber end facet by a unique direct coating method using the liquid solution, and another by transferring the SWCNTs from solution to solid, flexible, polymer film that is inserted into the laser cavity. Q-switching operation of the ring-cavity EDFL was achieved and documented in five discrete cases using three dissimilar SAs, each with their own interesting properties. The direct coating of a solution of SWCNTs in isopropanol causes Q-switching with both 3 and 10 layers of solution applied. The pulses formed in each instance have different temporal durations and are generated at different rates, but both are stable and have low noise. The 3-layer SA produces a higher repetition rate of shorter pulses with sharper peaks.

Wavelength spectra of these two Q-switching cases are not documented. Again, the direct coating method is used with a pristine solution of purified SWCNTs in DMF to make a two-layer SA. With this SA, stable pulse formation at two pump powers is seen, but have quite different properties. The lower of two pump powers induces pulsed operation that is much noisier, a smaller peak-to-peak voltage of less than 40 mV, longer pulse duration and broader pulse peaks. The higher pump power induces pulsed operation with close to 30% decrease in pulse duration while increasing the repetition rate by no more than 6%, the noise in the pulses is significantly reduced, and peak to peak voltage is increased to near 200 mV, an increase of over 400%.

The wavelength spectrums at each respective pump power also have considerable differences. At low pump power, there is a single narrow peak with a few small side lobes and low noise, and at high pump power there is a dual peak, each having larger FWHMs and more noise. The dual peak contains one peak no more than 1.09 nm lower than the single peak, and a second
peak another 38 nm lower than that. Each of the dual peaks has an average power of less than -10 dBm while the single peak approaches -5 dBm. The decrease in average power follows from the simultaneous decrease in pulse duration with static repetition rate. Considering the differences, it seems that this SA performed better overall at higher pump powers.

The behavior of pulses at lower pump power suggests that there is not enough light in the cavity to fully saturate the absorber. In the low light conditions, the absorber only partially saturates before it can reset. This partial saturation means partial transparency, which, in turn, causes the energy built up in the erbium fiber to only partially dump. Without enough light in the cavity to fully saturate the absorber, the oscillatory variation of the cavity loss due to the saturable absorber has a lower magnitude and slower response. Increasing the pump power to near maximum increases both the light inside the cavity and the amount of energy stored in the erbium fiber. The increased light circulating the cavity is capable of fully saturating the absorber, meaning its transparency is momentarily maximized, and the energy stored in the erbium fiber is fully dumped. As seen in Figures 5.4 and 5.5, this results in temporally shorter pulses that carry more energy. From this, one could conclude that SAs require a minimum photon flux to function at their maximum potential. Failing to meet this threshold results in small peak-to-peak oscillations around a more consistent roundtrip cavity loss, leading to inadequate pulse formation and a low-bandwidth frequency spectrum. Once the threshold is met or exceeded, the SA responds with a significantly larger dynamic range of cavity loss modulation, the cavity remains in a high-loss state for longer, and the sudden drop to low-loss followed by a rapid return to high-loss has markedly shorter duration.

Lastly, a SWCNT-PMMA polymer composite film is synthesized and inserted into the ring cavity. The performance of this SA is impressively better than the previous cases. The temporal
duration of output pulses drops dramatically to just over 700 ns, merely 26% that of the previously shortest pulses, and the repetition rate surges to over 142 kHz, an increase of over 373% compared to the next highest. The wavelength spectrum is quite broad and smooth, and has the highest bandwidth. This enormous improvement in device performance attests to its quality. Interestingly, though, the initial solution of SWCNTs in DPS is created using a bath sonicator and is not filtered. Therefore, the nanotubes are not well dispersed before being added to the MMA, yet the resulting SWCNT-PMMA film produces the best results for each measured property. The coexistence of these facts gives strong evidence to show the polymerization reaction transforming liquid MMA to solid PMMA causes disaggregation of SWCNT bundles and aids in their homogeneous dispersion throughout the polymer film.

Considering once more the SA creation techniques, after the dispersion of SWCNTs in an organic solvent, only two paths remain: direct coating and polymer synthesis. The performance of both direct coating SAs are similar to one another when compared to the results of the polymer SA, and they both perform rather poorly compared to the polymer SA. One direct coating SA is made with a low-quality dispersion, and the deposition of SWCNT material across the fiber ferrule is visibly random and patchy. The other direct coating SA is made with the most pristine solution I ever manufactured, and the deposition of SWCNT material is visibly distributed more evenly across a smaller area centered on the core of the fiber. Apparently, the direct coating method of SA creation works at about the same level regardless of the initial quality of SWCNT solution used to make it. The reason for this may be inherent to the process by which the SWCNTs are deposited onto the fiber end facet. The droplet of solution placed onto the end facet contains a set amount of SWCNTs. As the solvent evaporates, the volume over which the nanotubes are spread slowly
decreases. The reduction in volume brings the nanotubes closer to one another, where eventually the van der Waals forces cause them to re-bundle. This results in an increasing nanotube bundle size as the deposition of each layer progresses. It seems possible, therefore, that the transfer of SWCNTs from solution to laser cavity via the direct coating method unavoidably reduces the quality of the initial dispersion so much that the difference in quality of initial dispersion is rendered void. This is quite the opposite of the case of SWCNT polymer composite formation, whereby the transfer of SWCNTs from solution to solid polymer film actually increases the dispersion quality of the initial SWCNT solution.

6.2 Future Works

6.2.1 Improving the Pulsed Operation to Achieve Mode Locking

To date, the laser has been successfully Q-switched by two different SA creation methods, but has not been mode-locked. Since one of the primary purposes for this thesis is to build a fiber laser and have it operate in the pulsed regime, one obvious goal for future work is to achieve mode-locking operation. I believe the first step toward this is further investigation into the effectiveness, or lack thereof, in the EDF currently spliced into the ring-cavity in reference to mode-locking. The current EDF has a significantly high gain, which is good, but it also has an incredibly high doping concentration. This high doping concentration leads to more nonlinear effects such as multi-photon absorption. Under strong pumping conditions the EDF emits a large amount of visible radiation in the ‘green’ wavelength range, most of which leaks out of the fiber in all directions. Also, the high doping concentration allows high gain over short distances; so, only 44.5 ± 0.5 cm of EDF is needed to achieve a small-signal gain of 57.3 ± 0.6 dB/m. This short distance of EDF provides a rather negligible amount of anomalous chromatic dispersion compared
to the large amount of regular chromatic dispersion provided by the SMF used for the rest of the ring-cavity. This high value of positive chromatic dispersion is detrimental to mode-locking, as the mode-locked pulse is spread so much in time with a relatively small amount of cavity round trips, destabilizing in mere nanoseconds. A longer EDF with less doping provides more negative chromatic dispersion to match the positive chromatic dispersion of the rest of the cavity while simultaneously generating fewer unwanted nonlinear effects. Finally, the core of the current EDF is only 4 µm in diameter, while the remainder of the cavity is constructed with standard SMF with a core size of 9 µm. The splices at either end of the current EDF scatter much more light, therefore, than an EDF with an 8 or 9 µm core size would. This excess scattering is also detrimental to stable mode-locking operation. So, I believe the investigation into using a different EDF, with less doping concentration, more length, and larger core diameter is a reasonable starting point to work toward achieving mode-locked operation.

6.2.2 Better SA Construction Techniques and SA Characterization

The quality and repeatability of SA construction from solutions of SWCNTs is another important avenue of research to be undertaken by future students. The coatings of SWCNT material applied to the fiber end facets work in an occasional and arbitrary manner. There does not seem to be much of a pattern, some work and some do not. Once with a poor quality solution and once with a high quality solution. I am unable to quantify the differences between each attempt other than a visual inspection and whether or not Q-switching of the laser occurs. Further investigation into these coatings is needed. Characterization of the quality of each coating will help in determining the specific parameters that make a significant difference between one coating
working and one not. Using this information, better methods of applying the coating of SWCNT material can be devised and then tested. As for the case of the SWCNT-PMMA polymer composite, a more consistent method of creation is needed, where the resulting film qualities can be somewhat predicted by the starting quantities of each constituent ingredient. It may be useful to note these films can also be created with already-polymerized PMMA. Instead of a solution of SWCNTs in DPS being added to liquid MMA in which a polymerization process is then initiated, solid PMMA beads may be added to a solution of SWCNTs in DMF and subsequently sonicated. This method requires fewer steps and no polymerization initiator chemicals, resulting in fewer variables to control. This added simplicity could lead to easily repeatable rapid production of high-quality SWCNT-PMMA films.
LIST OF REFERENCES


APPENDICES

APPENDIX A:  CALCULATION OF MAXIMUM AVERAGE INTRA-CAVITY OPTICAL INTENSITY INCIDENT ON SWCNT SAs DURING Q-SWITCHING OPERATION

> with(Units[Standard]) :
>
> P_avg_out_meas_dBm := 0.74\cdot\text{Unit}(\text{decibels}) ;
    \[ P_{\text{avg \ out \ meas \ dBm}} := 0.74 \ [dB] \]
>
> output_coupler_90_10_loss := evalf(10\cdot\log10(9))\cdot\text{Unit}(\text{decibels}) ;
    \[ \text{output\_coupler\_90\_10\_loss} := 9.542425098 \ [dB] \]
>
> secondary_output_coupler_50_50_loss := evalf(10\cdot\log10(2))
    \cdot\text{Unit}(\text{decibels}) ;
    \[ \text{secondary\_output\_coupler\_50\_50\_loss} := 3.010299957 \ [dB] \]
>
> P_avg_intra_cav_dBm := P_{\text{avg \ out \ meas \ dBm}}
    + \text{output\_coupler\_90\_10\_loss}
    + \text{secondary\_output\_coupler\_50\_50\_loss} ;
    \[ P_{\text{avg \ intra \ cav \ dBm}} := 13.29272506 \ [dB] \]
>
> P_avg_intra_cav_mW := 10^{\left( \frac{13.29272506}{10} \right)}\cdot\text{Unit}(\text{milliwatts}) ;
    \[ P_{\text{avg \ intra \ cav \ mW}} := 21.34383751 \ [mW] \]
>
> r_{\text{SMF}} := 4.5\cdot10^{-6}\cdot\text{Unit}(\text{meters}) ;
    \[ r_{\text{SMF}} := 0.000004500000000 \ [m] \]
>
> intra_cav_cross_sec_area := evalf\left( r_{\text{SMF}}^2 \cdot \pi \right) ;
    \[ \text{intra\_cav\_cross\_sec\_area} := 6.361725124 \times 10^{-11} \ [m^2] \]
\[ \text{avg\_intra\_cav\_intensity} := \frac{P}{\text{intra\_cav\_cross\_sec\_area}} \]

\[ \text{convert( combine( 335503925.3 * Units::Unit( ('kg') / ('s')^3 ), 'units' )}, 'units', 'mW/m^2'); \]

\[ 3.355039253 \times 10^{11} \left[ \frac{mW}{m^2} \right] \]

\[ \text{convert( combine( 'units' ), 'units', 'kW/cm^2');} \]

\[ 33.55039253 \left[ \frac{kW}{cm^2} \right] \]