Carbon Nanotube Growth Via Spray Pyrolysis

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CARBON NANOTUBE GROWTH VIA SPRAY PYROLYSIS

by

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Thesis submitted in partial fulfillment of the requirements for the degree of

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in the Department of Physics

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Abstract

Spray pyrolysis is a promising method to create carbon nanotube forests (CNFs) on various surfaces. By injecting metalloocene-hydrocarbon solutions into a heated quartz reactor, catalyst particles and carbon nanotubes can be formed simultaneously. Factors that affect CNF growth include the precursor concentration, injection rate and duration, carrier gas flow rate, substrate surface, growth temperature, and the composition of gases inside the reactor. The CNF morphologies affected by these factors will be presented and, hopefully, an optimum condition will be found.
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1 Introduction

Materials with novel properties have become integral in modern society. Without these materials many forms of technology, from computers to modern traffic lights, would be impossible. As such there is a continuous search for new materials with novel properties that can improve modern technology. Carbon nanotubes (CNTs) are one of the candidate materials for such improvements. Thanks to the unique mechanical and electrical properties of the CNTs many applications have been thought up such as biological and chemical sensors, non-volatile memories, wiring, hydrogen storage, field emission, and electromagnetic shielding. In particular, low-density vertically aligned CNTs have been shown to have a total integrated reflectance of less than 0.045%, which is nearly 35 times lower than the NIST certified reference for optical reflection, and less than 0.2% in the mid-to-far-IR regime.\textsuperscript{1,2} This particular quality of CNTs suggests that CNT-covered surfaces can be used to house the sensitive imaging and positioning devices used in some space missions, because even a small amount of reflected light could affect sensitivity or create erroneous signals in such devices.

The Space Dynamics Laboratory (SDL) has funded research at Utah State University to investigate the growth of CNTs on conducting substrates – Cu in particular. If successful, this research will enable SDL to use CNTs in their orbital imaging instruments to reduce errors in the signal. The major challenge in this research is to control the length and density of the carbon nanotube forests (CNFs).

For a carbon nanotube to grow it first needs a nanoscale catalyst particle. Carbon atoms attach to the catalyst particle in a cylindrical fashion and create a tube which can be single-walled or multi-walled. When catalyst particles are closely arranged on a substrate, CNTs can grow in such a manner that they appear to form a “forest.” These carbon nanotube forests (CNFs) are generally grown on a substrate via a process called chemical vapor deposition (CVD). In CVD the catalyst particles are created either by depositing a nanometer-thick film before the growth or injecting liquid precursor during the growth (spray pyrolysis). CNT growth is conducted in a high temperature (often ~700ºC) reactor. The high temperature serves two purposes; it decomposes the various gases into its atomic constituents and it allows catalyst atoms to diffuse on the surface of the substrate to form the particles around which the CNTs will grow.

The in-diffusion of the catalyst particles is what inhibits the growth of CNTs on most metals. For example, iron atoms can diffuse 35nm into a copper substrate in 1s at 700 ºC.\textsuperscript{3} This rapid diffusion provides little time for iron atoms to form catalyst particles.

In order to grow a CNF many different factors must be controlled during the growth process. Several of the more important variables in CNT growth are substrate surface, growth temperature, ferrocene concentration, precursor injection rate and duration, carrier gas flow rate, and the ratio of reactant gases in the chamber. (These gases could be ammonia, hydrogen, water, ethylene, or others.) Fine-tuning these variables will determine the amount and types of CNT
growth as well as their growth rate.\textsuperscript{4,5} This study will investigate the effect of these different variables on CNT growth via spray pyrolysis CVD.

2 Theory

Ideally CNT growth is limited only by how much carbon is injected into the system because new carbon atoms will be able to react with catalyst particles and lengthen the nanotube. In reality that is not a simple state to achieve. An excessive amount of carbon or the presence of contaminants can quickly terminate growth by deactivating the catalyst particles. For example if too much carbon is injected amorphous carbon can begin to form on the substrate and eventually cover the catalyst particles. If the density of the CNF is too high the diffusion rate of carbon atoms to the surface, where the catalyst particles are, decreases dramatically nearly stopping the growth. If the ratio of reactant gases is not correct the hydrocarbons might not completely decompose leaving a shortage of carbon. In order to understand how to achieve continuous growth each variable in the experiment must be carefully considered.

There are two main facilitators for CNT growth; the nature of catalyst particle nucleation on the substrate and the deposition of carbon atoms onto the catalyst particles. All of the parameters in this experiment are meant to manipulate these two processes in a particular way. This section will review several of the variables that have proven to be important. Past studies that have examined these variables will be compared but unfortunately they do not always agree due to differences in reactor geometries, impurities in carbon feedstock, catalyst deposition methods, etc… Because the experimental setup in this study was used primarily for injection CVD, this overview will discuss the role of these parameters as they apply to that method.

2.1 Substrate

Growing CNFs on different substrates is important because many different materials are used in modern technology. Optimal interaction between the substrate and the catalyst particles is vital to a successful growth. Surface roughness influences the diffusion and growth of catalyst particles and the orientation of grown CNT.\textsuperscript{6} Surfaces can even be treated so that CNT only grow in specific regions on the substrate.\textsuperscript{7} Another important factor is how well the catalyst particles can diffuse on the substrate surface. In this study quartz (SiO\textsubscript{2}), silicon, and copper were investigated as substrates for CNF growth.

Quartz is one of the most common substrates used in CNF growth.\textsuperscript{6,8,9} It is so common because it requires very little preparation time and it is commonly used to make the reactor tubes for CNT growth. Silicon is also a common substrate perhaps because of its widespread use in technology. Silicon generally requires a barrier layer which is usually a thin (nanoscale) layer of SiO\textsubscript{2} (~500nm) due to thermal oxidation. In fact Zhang et al. reports that CNTs will not grow on pure silicon.\textsuperscript{7}
Metals are very difficult substrates for CNT growth. The problem is that the catalyst particles diffuse into the substrate rather than nucleate on the surface of the substrate. This diffusion prevents any reaction between the carbons and the catalyst particles. A common solution to this problem is to use a diffusion barrier (similar to the SiO$_2$ on silicon). Several different barrier layers have been tested for copper such as titanium nitride (TiN), silicon nitride (SiN$_x$), and indium tin oxide (ITO). Of those three only TiN has been shown to grow aligned CNT. Al$_2$O$_x$ has also been considered as a possible diffusion barrier and is used in this study.

Surface conditions such as cleanness, smoothness, and surface chemical reactions at the high growth temperature can also affect the catalyst particle nucleation and subsequently, CNF growth.

2.2 Reaction Temperature

The reaction temperature for growing carbon nanotubes is important for several reasons. It is the high temperature that breaks down hydrocarbons and allows catalyst atoms to diffuse on the surface of the substrate to create suitably sized catalyst particles. Several key characteristics of CNT growth are affected by those factors. Catalyst particle size (which is possibly important in CNT diameter), density of CNT growth, and CNT growth rate are all affected strongly by the growth temperature. Tapaszto et al. found that average CNT diameter increased with temperature until approximately 850°C and then average diameter began to decrease. This affect was attributed to the formation of single-walled CNTs – which have a much smaller diameter than multi-walled CNTs – above 850°C. Zhu et al. also suggests that temperature could determine whether CNT growth is reaction-rate controlled or diffusion-controlled. In these experiments it was found that temperatures that are too high can enhance polymerization of the carbon feedstock.

2.3 Ferrocene Concentration

Ferrocene dissolved in xylene is a common catalyst precursor for injection CVD. Low ferrocene concentration means that there will be fewer iron atoms to form catalyst particles on the substrate. This could mean that catalyst particle size will decrease with lower ferrocene concentrations. That result is confirmed by Singh et al. who found that CNT diameters and total carbon yield decrease with decreasing ferrocene concentration. However, an overabundance of carbon atoms may deposit on the catalyst or form other undesirable carbon structures at growth temperature if the concentration is too low.

2.4 Precursor Injection Rate and Duration

The nature of the injection of the ferrocene/xylene precursor strongly controls the growth of CNT. Injection rate determines how many particles are in the chamber at a given time reacting with each other. Injection duration controls how long the CNT will be, assuming that the
catalyst particles are not deactivated during the growth process. The carbon concentration in the tube is also highly dependent on the carrier gas flow rate and will be discussed below.

While injection duration is important in determining CNT height there is not always a linear relation between the two. The growth rate of CNT tends to decrease as reaction time increases. Several studies have provided evidence that this effect is due to the need for the hydrocarbon source to diffuse through the array of CNT that have previously grown and that the decay of the growth rate can be fit with a square root diffusion law.\textsuperscript{5,13,14} Other studies have called that result into question and attribute the decreased growth rate to gradual deactivation of the catalyst particles.\textsuperscript{11}

Prolonged injection stages can cause overgrowth material to deposit on the CNF. Singh \textit{et al.} suggests that this effect might be due to the continuous influx of iron atoms that deposit onto the CNT already present and provide catalyst particles for new growth.\textsuperscript{5} Pinault \textit{et al.} refutes this claim and attributes what appears to be overgrowth to an initial layer of entangled CNT that appears at the top of any CNT film.\textsuperscript{15}

\textbf{2.5 Carrier Gas Flow Rate}

The flow rate of the carrier gas mixture needs to be optimized to gain maximum growth. Similar to the injection rate, the flow rate is partly responsible for the carbon concentration in the tube, which is one of the two main factors in CNT growth. Carbon concentration ($C_{ci}$) in the tube can be calculated using Eq. 1 where $Q_c$ denotes injection rate of the feed solution (mL/min), $Q_{HI}$ is flow rate of the carrier gas (mL/min), $\rho_c$ is density of the liquid solution (g/mL), $n_c$ is the number of carbon atoms in one molecule of the carbon source in feedstock, and $M_{cs}$ is molecular weight of feedstock (g/gmol).\textsuperscript{9}

$$C_{ci} = \frac{Q_c\rho_c n_c}{Q_{HI}M_{cs}}$$

Malek \textit{et al.} found that there is an encapsulation concentration for $C_{ci}$. If $C_{ci}$ exceeds that value the CNT yield decreases significantly because of catalyst particle deactivation due to the formation of amorphous carbon.\textsuperscript{9}

CNT growth is slightly affected by the fact that the gas flow in the tube is not constant. Near the walls of the tube the gas flow is slower and the presence of a sample in the tube also disrupts flow. While this effect exists in most experiments it is generally not significant enough to be taken into account because of the high gas flow rate.\textsuperscript{5}

\textbf{2.6 Reactant Gases}

The mixture of different gases in the growth chamber has proven itself to be an important parameter in the quality of CNT growth. Generally an inert gas is used as the principal carrier gas. Other gases are included to perform tasks like etching the sample surface, improving CNT
purity, or providing additional carbons for CNT growth. For example Li et al. observed that injecting a small amount of air into the reaction chamber dramatically increased the lifetime of catalyst particles and allowed for extremely long growths.\textsuperscript{11} Other groups have found that when water vapor is injected into the system they obtain significantly longer growth and higher purity CNT.\textsuperscript{10,13,16}

Hydrogen is commonly used in spray pyrolysis CVD along with argon as the primary carrier gases. It has been proposed that hydrogen prevents the formation of amorphous carbon on the substrate surface and thereby extends catalyst particle lifetime.\textsuperscript{17} However there is conflicting evidence that shows hydrogen inhibits CNT growth.\textsuperscript{5} Zhang et al. even found that the role of oxygen in CNT growth is to provide a higher carbon to hydrogen ratio.\textsuperscript{18} In this study hydrogen is found to inhibit formation of polymers and larger metal crystals; both are helpful for CNF growth.

3 Experiment

3.1 Chemical Vapor Deposition

An injection chemical vapor deposition method was used for the experiments. The experimental setup is shown in Fig. 1.
In order to improve control of the reaction a new system was built that could be evacuated prior to growth and was well sealed to prevent any leaking. This new system uses a Thermolyne single zone split tube furnace with a quartz tube that has been fitted with Kwik flange attachments at both ends. Reactor pressure is measured using a Varian XGS-600 gauge. A vacuum-tight injector assembly (see Fig. 2) for the ferrocene/xylene solution was built for the system. An important feature of the injector assembly is the linear translation stage which is essential to keep the injector head within a particular temperature range to regulate the precursor vapor.

Samples were placed nine inches from the center of the tube furnace (the temperature at that position is still within 20°C of the temperature at the center) on a quartz or stainless steel boat. The quartz tube reactor is first evacuated and then backfilled with pure argon. As the furnace is heated the flow of argon is kept at approximately 50 sccm. When the injector head reaches 170°C (generally the furnace temperature has been stable for 5-10 min by that time) the argon flow rate is increased to 100 sccm and a mixture of ferrocene dissolved in xylene is rapidly injected (approximately 20 ml/h) until the solution reaches the injector head in order to reduce the amount of xylene that is prematurely evaporated. Once the solution reaches the injector head the injection rate is reduced to approximately 4 ml/h with various argon flows. When the solution is depleted the syringe is withdrawn to remove the remaining solution in the injector line and argon flow rate is increased to 100 sccm and the furnace is turned off to prevent further reaction in the system.

Copper substrates required an extra preparation step. In order to prevent diffusion of the catalyst particles into the substrate copper samples were coated with a layer of aluminum (5-15 nm) that was oxidized to a depth of 2-3 nm. Aluminum oxide is an excellent insulator and proved to be an adequate diffusion barrier in these experiments. The aluminum layer was deposited using a home-made thermal evaporation system.

3.2 Experimental Parameters

Key parameters in this experiment are the carrier gas composition and flow rate. Flow rates from 50 to 300 sccm during growth were tested. Injection of small amounts of water and
hydrogen during precursor injection were tested. Various injection rates, concentrations of ferrocene, and growth temperatures were also examined.

Substrate surface roughness was characterized using a PSIA XE-100 atomic force microscope. Atomic force microscopy (AFM) utilizes a silicon tip which interacts with the surface via contact or non-contact mode. In contact mode the tip is driven towards the surface until it measures a given set force. The tip is then translated over the surface at constant force to create a topographical map of the substrate. Non-contact mode keeps the tip farther from the surface and measures the interaction force by vibrating the tip at a resonant frequency and measuring the changes in frequency as the tip is translated over the substrate. Scanning electron microscopy (SEM) was used to image samples after CNT growth.

AFM data was taken for copper samples prepared under different conditions. These conditions included annealed vs. un-annealed and pure copper vs. copper with an alumina layer. In order to investigate the role of surface roughness on CNT growth many experiments were done with quartz samples that had been etched with hydrofluoric acid (HF). The roughness of these samples was characterized using AFM.

4 Results

4.1 Catalyst Particle Delivery

One of the two major challenges in CNF growth is to control the distribution of catalyst particles. In spray pyrolysis catalyst particles are deposited on the substrate by thermal decomposition of injected metalloocene molecules followed by adatom diffusion and nucleation on the surface. In this study ferrocene \([\text{Fe(C}_5\text{H}_5\text{)}_2\text{] dissolved in xylene (C}_8\text{H}_{10}\text{) serves as the source for both catalyst and carbon feedstock. With a carrier gas flow rate of 100 sccm, the Fe particle distribution is visible from 2.75” from the injector to 25.25” after oxidation in air. (Fig. 4a) Fe particle density is clearly higher in the first 5.5” of the tube. Thus, changing the position of the sample in the reactor tube can be a control on the catalyst particle density.

![Fig. 3 – PSIA XE-100 Scanning Probe Microscope](image)

![Fig. 4: (a) Oxidized Fe particle distribution on the reactor wall by ferrocene/xylene precursor swept by a carrier flow rate of 100 sccm. (b) Oxidized Fe particle distribution on the reactor wall by ferrocene vapor swept by a carrier flow rate of 200 sccm.](image)
It is also possible to supply the Fe particles by ferrocene sublimation. Figure 4(b) shows the result of a crude test where a ferrocene vapor was swept through the tube by an argon flow of 200 sccm while keeping the ferrocene source below 140 ºC. The oxidized iron distribution is visible only in a section of 6”.

The CNFs grown from these two methods are compared in Fig. 5. Liquid precursor injection (Fig. 5a) clearly leads to a denser CNF than the solid ferrocene vapor does (Fig. 5b).

4.2 Decomposition of Ferrocene

For each iron, ferrocene provides 10 carbon atoms; a 10-nm diameter iron particle could contain $10^3$ iron atoms. One thousand iron atoms would need the same amount of ferrocene molecules which come with $10^4$ carbon atoms. With so much carbon the question is will that be sufficient to initiate CNT growth? In this study after ferrocene vapor deposition, the front 5” of reactor wall is blackened by carbon, but the rest of the reactor remains clear. Although we do not know the nature of this carbon film, we know it stopped abruptly at the higher temperature region of the reactor, independent of the Fe distribution. It has been suggested that at temperatures greater than 500 ºC, ferrocene is decomposed into a slew of products including Fe, H$_2$, CH$_4$, and C$_5$H$_6$. Figure 4(b) confirms that Fe has been dissociated and deposited on the reactor wall. It is possible that cyclopentadienyl (C$_5$H$_5$) is only partially decomposed in the reactor leaving insufficient carbon feedstock to grow CNTs farther than about 5” into the reactor. CVD growth was carried out, without cleaning, out by using ethylene (C$_2$H$_4$) as the carbon source and Ar with 50% H$_2$ as the carrier gas. Visible carbon deposition in this case extended to 14” on the reactor wall. (Fig. 6) In another experiment, it was observed that pure ethylene does not result in carbon deposition on quartz at 700 ºC. Combining these results shows that iron catalyst particles can be invisible to the naked eye even if they are oxidized and with sufficient carbon and hydrogen, carbon can be grown on anywhere with iron particles.

Fig. 6: Carbon deposition after Fig. 3(b) by a CVD of ethylene (25 sccm), H2 (25 sccm) and Ar (50 sccm) at 700 ºC
4.3 The Critical Role of $H_2$

Similar to ferrocene, xylene cannot be decomposed directly to individual carbon and hydrogen atoms at high temperatures. In the presence of $H_2$ a chain of reactions from xylene to toluene ($C_7H_8$), benzene ($C_6H_6$), and methane has been suggested. Benzene can be further decomposed to acetylene ($C_2H_2$) from which hydrogen can be stripped upon interaction with the catalyst particles leaving carbon dimers to be incorporated into CNT. Without sufficient hydrogen, polymerization of hydrocarbons will occur at high temperatures. Our experiments show that when injecting xylene at a rate of 4 ml/h, a gas mixture of Ar: $H_2$=75:25 sccm leads to yellowish to reddish precipitation at the exhaust end of the reactor outside the furnace, but a gas mixture of Ar: $H_2$=50:50 does not. By reducing the xylene injection rate to 2 ml/h, hydrogen flow rate can be reduced to 25 sccm without observing this polymer precipitation. However, increasing the furnace temperature to 750 °C resulted in the same condition precipitation. (Fig. 7) This result suggests that with the same amount of hydrogen input, higher temperature enhances polymerization more than pyrolysis. At 750 °C a flow of 25 sccm of pure ethylene can also exhibit this polymer precipitation but it can be counteracted by replacing 10 sccm of $C_2H_4$ by $H_2$. These results demonstrate the importance of $H_2$ in the hydrocarbon pyrolysis.

We have also observed that without proper $H_2$ in the reactor, spray pyrolysis of ferrocene/xylene precursor leads to the formation of a reflective crust with CNF grown on the underside. (Fig. 8) While the exact composition of the crust and the formation mechanism are unclear at this point it is probably a high carbon, low iron mixture. The crust remains intact after dipping in hydrochloric and sulfuric acid but is burned off easily by a flame suggesting the above mixture.
Several tests were carried out in attempts to avoid the formation of this crust. Increasing the carrier gas flow rate from 50 to 300 sccm, decreasing the ferrocene concentration in xylene from 6 to 1.5 mol %, decreasing the precursor injection rate from 4 to 2 ml/h, and decreasing the total precursor dose from 1.2 ml to 0.2 ml all resulted in the same reflective crust. Eventually, a dense uniform CNF was created by adding 50% H₂ in the carrier gas. (Fig. 9) We also found success in CNF growth by using a gas mixture of Ar:H₂:C₂H₄=50:25:25 on a surface coated with iron similar to Fig. 4. It is possible that too much hydrogen may suppress the pyrolysis of methane to atomic carbon, but further study is required in that regard.

At high temperatures hydrogen can also interact with the substrate surface and affect the CNT growth. Figure 10(a) shows CNTs peeled off from the quartz substrate after being annealed in hydrogen at 700 °C perhaps due to SiO₂ etching by H₂. Similarly, CNT growth is greatly suppressed in hydrogen rich environments on Si substrates. Again, probably because the native oxide on the substrate is etched off by H₂. Figure 10(c) shows CNT growth on Si substrate without H₂ in the carrier gas.

To facilitate CNT growth on copper, we have coated the copper surface with a 6-15 nm thick layer of aluminum as the diffusion barrier for the Fe atoms. An oxide layer of 2-3 nm will be formed subsequently in air or in a pure O₂ environment. At 700 °C, the copper might diffuse through the liquid aluminum and oxide barrier to form crystals on the surface (Fig. 11a) resulting in bare spots in later CNF growth. However, when annealing the Al/Cu sample in an Ar:H₂=2:1 environment, no Cu crystals can be found (Fig. 11b) and a uniform CNF is grown. (Fig. 11c)
4.4 Surface conditions

For CNT growth to work iron atoms need to diffuse on the substrate surface and nucleate into nano-scale particles. CNT growth will be inhibited if the iron atoms are immobilized by surface chemical reactions or diffuse into the substrate. Besides chemical reactions, at 700 ºC, bulk and surface phase transition may occur resulting in different surface morphologies. Figure 12a shows that CNTs only grow on defect sites of copper surfaces, but an aluminum oxide layer, as described in the previous section, could serve as a diffusion barrier for iron and allow uniform CNF growth. At room temperature, only the top 2-3 nm of aluminum are oxidized. During CNT growth at 700 ºC, the aluminum film underneath the oxide layer melts cracking the thin oxide crust (Fig. 12b) and leading to the intriguing but poorly understood CNT formation shown in Fig. 12c.

We also noted that solvent cleaning cannot ensure a uniform CNF on quartz surface, but a 20s dip in 10% aqueous HF solution can. Etched samples have a root mean square roughness approximately ten times that of un-etched samples. It is not clear if the growth improvement is due to the HF etch roughening up the surface (Fig. 13) or removing surface contaminants.
Conclusions

Carbon nanotube growth using a spray pyrolysis method is highly dependent on many different parameters. This sensitivity makes it challenging to optimize the system to obtain sustained CNF growth. Due to this complication the literature on growing CNF via spray pyrolysis occasionally conflicts with itself. Frequently growth parameters provided in the literature cannot transfer between systems that have different geometries or impurities.

Unlike deposition CVD, which requires an extra metal deposition step, spray pyrolysis method allows a user to grow CNFs using on single CVD system. This simplicity is possibly the culprit for the many optimization problems in the spray pyrolysis method. Iron atoms are depositing on the surface and forming catalyst particles at the same time carbon atoms are reacting to iron catalyst particles and forming CNT. When hydrogen and other reaction gases are included it makes the system even more uncontrollable. The solution to these problems is to understand each growth parameter and carefully control the system. The goal of this research is to achieve sustained CNF growth in this system and obtain sufficient control over the density of CNF so that it can be used to absorb far infrared radiation.

5.1 Future Work

As was shown here hydrogen concentration in the reactor tube is essential to obtain vertically-aligned CNTs with the spray pyrolysis method. Further optimization of hydrogen concentration will provide a steady stream of carbon atoms to contribute to CNT growth.

Another common obstacle in CNT growth is the formation of amorphous carbon on the substrate surface. This amorphous carbon can gradually cover the catalyst particles and terminate growth. In the literature it has been shown that injecting a small amount of water vapor can clean the amorphous carbon off the substrate and extend catalyst particle life. Finding the correct amount of water vapor to inject could be an important part of future research with this system.

Fig. 13: (a) AFM image of the fused quartz surface. (b) Quartz surface after 20s dip in 10% aqueous HF solutions
References


Author’s Biography

Robert Call grew up in rural Batesville, Indiana and graduated from Batesville High School in 2005. He came to Utah State University as an Undergraduate Research Fellow studying Physics with a Professional Emphasis. After his first year at USU he took a brief leave of absence to serve a mission for the LDS church in the Dominican Republic. After returning in fall 2008 he continued in Physics and will graduate in spring 2011. As an undergraduate he had the opportunity to work as a summer intern at Lawrence Livermore National Laboratory in their Condensed Matter and Materials Division as well as numerous research opportunities at USU. In 2010 he was named a Goldwater Scholarship Honorable Mention. In August 2010 he married Heather Noel Studer.

Robert intends to pursue a Masters degree in physics at USU following graduation. After his Masters he intends to do Ph.D. work in anything that will get him involved with alternative energy. He hopes to one day be involved in applying new alternative energy technologies to society.