THERMIONIC EMISSION OF DIAMOND USING LASER AS A HEAT SOURCE

By

Ian Ly Davis

Thesis

Submitted to the Faculty of the

Graduate School of Engineering of Vanderbilt University

in partial fulfillment of the requirements

for the degree of

MASTER OF SCIENCE

in

Electrical Engineering

May, 2007

Nashville, Tennessee

Approved:

Dr. Bo K. Choi

Dr. Weng P. Kang

TABLE OF CONTENTS

	Page
IST OF TABLES	iii
IST OF FIGURES	iv
hapter	
-	
I. INTRODUCTION	1
II. THEORETICAL BACKGROUND	2
Thermionic Emission	2
Field Emission	4
Energy Conversion Efficiency	6
Physical Properties of Diamond	6
Fundamentals of Laser Physics	7
Pulsed Laser and Q-switching	8
The Nd:YAG Laser	9
Heat Transfer	9
Temperature Calculations	10
III. EXPERIMENTAL SETUP	15
Setup Process	15
Vacuum Chamber	16
Circuit Setup	17
Laser Setup.	20
IV. RESULTS AND DISCUSSION	22
Preliminary Testing	22
Schottky Effect	24
Current-Temperature Relationship	26
Conversion Efficiency	
Ionization Effects	32
V. CONCLUSION	
REFERENCES	37
ADENIDIY	20
ΑΓΓΕΝΟΙΑ	

LIST OF TABLES

Ta	ble	Page
1.	Comparison of Diamond and Silicon	7
2.	Parameters of Laser Equations (Silicon)	12
3.	Conversion from Energy to Peak Temperature	13

LIST OF FIGURES

Figu	ure	Page
1.	An example Schottky plot	3
2.	An example plot of Fowler-Nordheim field emission	5
3.	Lattice temperature distribution	14
4.	Photograph of the resistor box	15
5.	Photograph of the mini-chamber with vacuum tube attached	16
6.	Circuit Drawing	17
7.	Vertical side view diagram of the setup showing the emission site	18
8.	Overhead drawing of anode and cathode	19
9.	Photograph of anode and cathode	19
10.	A photograph of the setup	21
11.	Pulsed laser light entering the min-chamber	21
12.	Field Emission I-V Characteristic	23
13.	Fowler-Nordheim plot. Units of current are in nA, while units of F are in $V/\mu m$	123
14.	I-V curve for each device	25
15.	Plot of natural log of current versus square root of voltage (Schottky)	25
16.	A plot showing the raw data of current versus lattice temperature	27
17.	a) Arrhenius Plot of temperature versus current using 300 K parameters b)using 1400 K parameters.	28
18.	Adjusted Arrhenius Plot	30

CHAPTER I

INTRODUCTION

Thermionic emission is a process by which electrons at the surface of a material can gain sufficient energy to escape the vacuum energy level and can contribute to emission caused by heating. Diamond is a natural insulator that can be used as a semiconductor given the right doping. As a semiconductor it displays key advantages over the widely used semiconductor silicon. It has electrical properties such as higher carrier mobility, higher breakdown voltage, low electron affinity and work function as well as physical properties such as higher thermal conductivity, higher strength and hardness, and higher melting point compared to silicon. Diamond also has a higher band gap than silicon, requiring more energy for electrons to reach the conduction band. Two devices, silicon and diamond on silicon are tested for thermionic emission properties. This thesis presents a method for efficient thermionic emission of diamond by taking advantage of its low electron affinity and work function and the known electrical properties of silicon. The energy conversion efficiency of this system is explored.

CHAPTER II

THEORETICAL BACKGROUND

Thermionic Emission

Thermionic emission is the release of electrons from a heated surface into a vacuum[1]. In circuits the surface of a material can be used as a cathode, and when all the emitted electrons are collected the cathode is said to give saturated emission and is written as the saturated current density J_s . Richardson's equation, derived by British physicist Owen Willans Richardson and first published in 1901 [2], expresses J_s in terms of the cathode temperature T and the work function ϕ , the minimum energy required for an electron to escape the surface of a material and drawn as the distance from the Fermi level to the vacuum level on an energy band diagram. The value of the work function is a property of the material. Richardson's equation is written

$$J_s = AT^2 \exp\left(-\frac{\phi}{kT}\right) (1)$$

where k is Boltzmann's constant and A is a constant having a value of

$$A = \frac{4\pi \times emk^2}{h^3} = 1.2 \times 10^6 \text{ Am}^{-2} \text{degree}^{-2} (2)$$

where e and m are the charge and mass of an electron and h is Planck's Constant. The effect of temperature on current density increases dramatically at high temperatures due to the temperature variable in the exponential driving the exponential toward unity and giving the equation a quadratic nature. The effect of differing values of electric field strength is ignored in this equation as it assumes that the voltage level is kept constant.

The first form of Richardson's equation would suggest that current emission is not dependent on the field strength of the cathode, but experiments show that electric field also plays a role in determining the saturated current density; emission current increases with an increase in electric field strength [1]. The Schottky effect, named for physicist Walter Schottky who first predicted the phenomena, describes the dependence of current density on electric field strength [3] and can be written:

$$J_{s} = J_{s0} \exp\left[\frac{e(3.79 \times 10^{-5}) \times \sqrt{F_{0}}}{kT}\right] (3)$$

where J_{s0} is the value of the saturated current density with no applied electric field, and therefore derived directly from the first form of Richardson's equation. Plotting $\ln(J_s)$ $\sqrt{F_0}$ gives a linear curve like the one shown in Figure 1. Extrapolating the linear part of the curve to a field strength of zero will give the value of J_{s0} [1].



Figure 1. An example Schottky plot [1]

Field Emission

Field emission, or Fowler-Nordheim tunneling, refers to electron emission due to the presence of a high electric field[4]. At high field strengths at the surface of the cathode, the potential barrier becomes thin enough to create a finite probability of having an electron pass through the surface barrier and emit as current[1]. This is called the tunnel effect and refers to the electrons "tunneling" their way through the surface barrier. Field emission occurs independently from thermionic emission, which depends on temperature. Since it does not depend on temperature, field emission is not a focus of this experiment, but serves as a preliminary test to ensure the proper function of the device.

The Fowler-Nordheim equation relates current density J_{FN} to electric field F. By applying the Wentzel-Kramers-Brillouin approximation, which ignores the temperature influence and lowering of the barrier by the Schottky effect [5], the Fowler-Nordheim equation can be written

$$J_{FN} = \frac{C}{\phi} F^2 \exp\left(-B\frac{\phi^{\frac{3}{2}}}{F}\right) (4)$$

where C and B are constants that depend on the density of the material in question and the shape and aspect ratio of the cathode, and ϕ is the work function. For this example the constants were set equal to one and the work function was set to 5 eV; the actual values of the constants are not relevant because only the slope of the curve is necessary to prove field emission. An example of field emission is show in figure 2. When the natural log of the current divided by the square of the voltage is plotted against the inverse of voltage, the plot shows a negative linear slope. When experimental current and voltage are plotted in this manner, a negative and linear slope indicates the field emission phenomenon.



Figure 2 An example plot of Fowler-Nordheim field emission

Energy Conversion Efficiency

Energy conversion efficiency is a ratio of the output of energy to the input of energy in a given system. In this experiment the input energy is the laser energy in the form of heat and the output is found from the current through the output resistor. Energy efficiency is a number between 1 and 0 and is an indicator of performance in a system.

Physical Properties of Diamond

Diamond is carbon arranged in a tetrahedral structure in which each carbon atom is covalently bound to its four nearest neighbors by sp^3 bonds. Diamond is an insulator in its naturally occurring form (resistivity of $10^{12} \Omega$ cm), but can be given semiconductor properties through doping. By doping with boron, diamond can be made into a p-type semiconductor[6]. Table 1 shows several properties of diamond side by side with the more familiar properties of silicon. Notably, diamond has higher carrier mobility than silicon while having a small, near zero work function. Physically, diamond is known as the hardest naturally occurring substance, scoring a 10 on the Mohs scale of hardness [7]. In comparison, silicon scores a 6.5 [8]. The melting point of diamond is also much higher than silicon, making its use desirable at extreme temperatures.

Property	Silicon	Diamond
Density (g/cm ³)	2.329 [8]	3.52 [7]
Thermal Conductivity (W/cm*K @ 25° C)	1.3 [9]	25 [6]
Atomic Density (cm ⁻³)	5 x 10 ²² [10]	1.77 x 10 ²³ [6]
Hole Mobility (cm ² /V-sec)	450 [10]	1500 [6]
Electron Mobility(cm ² /V-sec)	1400 [10]	1800 [6]
Band Gap (eV)	1.12 [10]	5.47 [6]
Work Function (eV)	4.5 [8]	Small [7]
Melting Point (K)	1687 [11]	4500 [6]
Dielectric Constant	11.8 [7]	5.68 [7]

Table 1. Comparison of Diamond and Silicon

Fundamentals of Laser Physics

For the purpose of this experiment, a laser is used as a heat source to increase the temperature at the surface of the material. Laser is an acronym which stands for Light Amplification by Stimulated Emission of Radiation, and is generally a device by which a beam of light, or laser beam, is generated by a lasing medium having several specific properties. Laser light differs from normal light in three key ways. First, while normal light can consist of many different colors on the visible light spectrum, a laser is monochromatic, having a specific wavelength and color. Laser is also coherent, organized in a beam where the photons move in a non-random, step-like manner. Finally, laser is directional. While normal light will shine and illuminate in all directions, laser light travels in one direction only and is much more focused than normal light[12].

Laser works through a medium in which electrons are excited, giving off energy and light in the form of photons, the basic units of electromagnetic radiation. Photons have no mass and have energy directly proportional to their wavelength, as shown by the equation E = hv where h is Planck's constant and v is the photon frequency [12]. In order to excite the electrons into a high energy state, the laser must be "pumped" by an outside energy source, usually by flashes of intense light or electrical discharge. Laser works with two mirrors, one at each end of the lasing medium. The photons created by excited electrons reflect off of the two mirrors to travel back and forth through the medium. In the process, they stimulate other electrons to make the downward energy jump and can cause the emission of more photons of the same wavelength and phase. A cascade effect occurs, and soon there are many photons of the same wavelength and phase traveling back and forth through the medium[13]. One of the mirrors is totally reflective (the HR or "highly reflective" mirror) while the other is partially reflective (the OC or "output coupler"). The laser light is released through the partially reflective mirror at a specific wavelength.

Pulsed Laser and Q-Switching

There are two types of laser with concern to the beam: continuous wave and pulsed laser. A pulsed laser can attain much higher peak powers than a continuous wave laser. One such method of pulsing the laser is Q-switching, which refers to pumping the lasing medium to a high energy state in the form of photons and suddenly releasing this energy in one short laser pulse [14]. This is accomplished by effectively removing the HR mirror so that lasing does not occur. When the photons have reached a desirably high or maximum energy state, the HR mirror is returned to place, and the normal lasing process can occur with the maximum energy. The laser is pulsed by manipulation of the mirrors controlled by a modulator or a passive semiconductor device. The high energy pulse can be used to rapidly heat a material, such as in the case of this experiment.

The Nd:YAG Laser

The neodymium doped yttrium aluminum garnet laser (Nd:Y₃Al₅O₁₂) is the laser used specifically for this experiment. The Nd:YAG laser is widely used for many different applications including medical surgeries, hair removal [15], and welding. Many of these applications typically operate at a wavelength of 1064 nm, in the infrared range. For the purposes of this experiment it is used as a heat source and operates at a wavelength of 532 nm and produces visible green light. The energy of the laser is converted to heat which transfers to the test material.

Heat Transfer

Since it is difficult to physically measure the exact temperature at the surface of a material inside of a vacuum chamber using a device, it is necessary to calculate the temperature using the heat transfer equation[16]. Heat transfer in a given material is based on the heat transfer equation

$$\frac{\rho C \partial T(r,t)}{\partial t} = K \nabla^2 T(r,t) + S(r,t)$$
(5)

where ρ is the density of the material, C is the specific heat, K is the thermal conductivity of the medium material, and S is the source heat. The variables *T*, *r* and *t* are temperature, distance and time, respectively. This creates a LaPlacian temperature gradient including

physical property coefficients that vary depending on the material in question[16]. For the purpose of this experiment the pulsed laser is used as the heat source which increases in magnitude as the number of pulses increases and the material is silicon. The total laser energy that contributed to the heat source was measured by a laser sensor.

Mathematical Calculation of Temperature at the Surface

The temperature at the surface of the diamond on silicon cathode comes from the heat transfer equation. Using the LaPlace transform iteratively and through a series of lengthy algebraic steps the temperature at the surface can be written directly in terms of distance and time [17]. Setting the recession velocity equal to zero gives the conduction limited heating case [18], as seen in equation 6.

$$T(x,t) = \frac{2I_0}{k} \sqrt{\alpha t} \times ierfc \left(\frac{x}{2\sqrt{\alpha t}}\right) - \frac{I_0}{k\delta} \exp(-\delta x)$$
$$+ \frac{I_0}{k\delta} \exp(\alpha \delta^2 t - \delta x) \times erfc \left(\delta \sqrt{\alpha t} - \frac{x}{2\sqrt{\alpha t}}\right) \quad (6)$$
$$+ \frac{I_0}{2k\delta} \exp(\alpha \delta^2 t + \delta x) \times erfc \left(\sqrt{\alpha t} - \frac{x}{2\sqrt{\alpha t}}\right)$$

The erfc function seen in the conduction-limited heating equation is the complementary error function and ierfc is its integral form [19] given by

$$ierfc(x) = \int_{\infty}^{x} erfc(s) ds$$
 (7)

and rewritten as

$$ierfc(x) = \frac{1}{\sqrt{\pi}} \left[exp(-x^2) - x(1 - erf(x)) \right]$$
(8)

where erf is the error function related to erfc by

$$erfc(x) = 1 - erf(x)$$
 (9)

Using Mathematica, simulations were run to show the effect of a constant laser and a pulsed laser on temperature. The pulsed laser allows for a higher energy and temperature at the surface, and a cooling effect between each pulse. The pulsed case was modeled based directly off of the original heat transfer equation. These output plots are an estimate of the temperature and are not exact, as thermal diffusivity and thermal conductivity change with rising temperature. To account for this, simulations were run for thermal diffusivity and thermal conductivity values at temperatures of 300 K and 1400 K [9]. Each calculated laser energy from the experiment was converted into a maximum temperature at the surface of the silicon. A pulse frequency of 10 Hz was used, so after each pulse, spaced one tenth of a second apart, a cool-down time was experienced. The constants used to make each plot reflect the values of silicon and are shown in Table 2. The laser energy was measured using a sensor and converted to units of Wm⁻² algebraically.

Parameter	Value	Reference
α (Thermal diffusivity) @300K	$8.6 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$	[9]
α (Thermal diffusivity) @1400K	$1.2 \text{ x} 10^{-5} \text{ m}^2 \text{ s}^{-1}$	[9]
δ (Absorption Coefficient)	$6.8 \times 10^5 \text{ m}^{-1}$	[20]
<i>k</i> (Thermal conductivity) @ 300 K	$156 \text{ W m}^{-1} \text{ K}^{-1}$	[9]
<i>k</i> (Thermal conductivity) @ 1400 K	$24 \text{ W m}^{-1} \text{ K}^{-1}$	[9]

 Table 2. Parameters of Heat Equation (Silicon)

A table of laser energies and the corresponding peak temperatures was made from the results of the simulation, seen below in table 3. A sample output, using laser energy of $3.00 \times 10^{11} \text{ Wm}^{-2}$ is shown in figure 3. The values from the plots are in degrees Celsius; the final values used in all further calculations are in degrees Kelvin. From the result of the plot in figure 3b, the temperature peaks near 30 nm below the surface and quickly cools down. The Mathematica source code used to construct the curves can be found in the appendix. Thermal heating of diamond was not measured because it was unnecessary due to the way the diamond on silicon device was heated. The silicon was 500 µm thick, and the heating effect of the laser lasts to less than 1 µm. The diamond does not feel and heating effects from the laser, but electrons that gain enough energy from the surface of the silicon can travel to the diamond and be released as emission there.

Laser Energy	Peak Temperature (300 K Parameters)	Peak Temperature (1400 K Parameters)
$3.00 \text{ x } 10^{11} \text{ Wm}^{-2}$	1300 K	1450 K
$4.12 \text{ x } 10^{11} \text{ Wm}^{-2}$	1600 K	1750 K
$4.80 \ge 10^{11} \text{ Wm}^{-2}$	1900 K	2100 K
$5.05 \text{ x } 10^{11} \text{ Wm}^{-2}$	1950 K	2150 K
$6.47 \text{ x } 10^{11} \text{ Wm}^{-2}$	2400 K	2800 K
$7.32 \text{ x } 10^{11} \text{ Wm}^{-2}$	2500 K	3050 K
$8.96 \text{ x } 10^{11} \text{ Wm}^{-2}$	3100 K	3500 K
$9.83 \times 10^{11} \text{ Wm}^{-2}$	3300 K	3900 K
$1.19 \text{ x } 10^{12} \text{ Wm}^{-2}$	4100 K	4400 K
$1.21 \text{ x } 10^{12} \text{ Wm}^{-2}$	4200 K	4500 K

 Table 3: Conversion from Energy to Peak Silicon Lattice Temperature



Figure 3. Lattice temperature of silicon distribution for input laser energy of 3.00×10^{11} Wm⁻² using 300 K parameters. a) Temperature versus distance and time and b) Temperature versus distance with time fixed at one pulse length.

CHAPTER III

EXPERIMENTAL SETUP

Setup Process

Before the final experiment could be performed a series of setup steps had to be taken. First, several BNC cables were manually created to an appropriate length so connections could be easily made between parts of the final circuit. A "resistor box" was created to easily maintain the circuit and allow any connections needed to be implemented quickly such as an oscilloscope, a multimeter, or capacitors. The resistor box was made using 1.5" screws and heat-wrapped wires with ring connectors soldered to the end for easy connection. A picture of the resistor box can be seen below. After the resistor box was completed, the vacuum chamber needed to be created. This chamber would serve to hold the test material while allowing for laser testing.



Figure 4. Photograph of the resistor box

Vacuum Chamber

The vacuum chamber was created using stainless steel parts. A decision was made to use a smaller, "mini-chamber" to conduct the experiment. Each part of the chamber was carefully cleaned in a boiling acetone bath and rinsed in a boiling propanol bath. The chamber was a cube consisting of six detachable sides. Each side was firmly attached using steel screws. The six sides of the chamber were two glass windows used for observation and laser exposure, a solid metal base, two electrical connection sides providing the anode and the cathode for the diode, and a hole that attached to the vacuum pump.

The vacuum pump keeps the pressure inside of the chamber at a level of 10^{-4} torr, a level acceptable to be close enough to true vacuum conditions to avoid plasma-induced emission from the air.



Figure 5. Photograph of the mini-chamber with vacuum tube attached

Circuit Setup

The experimental circuit is simply a diode connected to a high voltage source with a resistor and ground. The diode itself sits in the vacuum chamber where its anode is connected to the source by a copper wire on the outside of one of the chamber's attached side. The cathode connects by a high voltage tolerant wire inside the chamber. Outside of the chamber the cathode is protected by several layers of high voltage electrical tape where a BNC cable is connected to the resistor box to complete the circuit. The resistor box itself contained a protective cover to protect against surges of current. The resistor used throughout the experimental process was 500 Ω . The current was calculated by measuring the voltage dropped across this resistor and using Ohm's law.



Figure 6. Circuit Drawing

The cathode was mounted on top of a layer of alumina and held in place by copper tape. It was slanted downward so that the tip would be underneath another piece of alumina sitting on top of the aluminum anode. Figure 7 shows a side view of how the laser light hit the surface of the silicon. The emission site was at the tip of the sample. The silicon thickness was 500 μ m, and the diamond thickness was approximately 3 μ m. The vacuum distance from the cathode to the anode was estimated to be from 700-1000 μ m. A piece of alumina was used to shield the emission site from direct exposure to the laser to ensure that any emission would be a result of energized electrons traveling the width of the top silicon layer. Figure 8 is a drawing of the overhead view and figure 9 is a photograph of the physical anode and cathode.



Figure 7. Vertical side view diagram of the setup showing the emission site



Figure 8. Overhead drawing of anode and cathode



Figure 9. Photograph of anode and cathode

Laser Setup

The laser used in this experiment is the Nd: YAG (neodymium doped yttrium aluminum garnet) laser operating in Q-switched pulsed mode with a wavelength of 532 nm and operating at a frequency of 10 Hz. The laser is a product of Continuum with product name Powerlite 9000 Series. When conducting the laser experiment the mini-chamber was held firmly in place by screws. The laser entered the glass window at the front of the mini-chamber. A picture of the setup can be seen in figure 10 and laser entering the mini-chamber can be seen in figure 11. The laser was operated by Shengteng Hu and provided by Dr. Robert W. Pitts, chairman of the department of mechanical engineering at Vanderbilt University.

The sensor used to measure the laser energy was a J50 model made by Coherent. The J50 larger area (50 mm) sensor provides a broad spectral response and high repetition rates. The detector diameter of the model is 52.1 mm with an area of 21.3 cm² [21]. A multimeter was used along with it to measure the voltage across the sensor as the laser was pulsing. From there the laser energy could be calculated.



Figure 10. A photograph of the setup. The front window of the mini-chamber faces the optical lens where the laser passes through. The lens controls the focal point of the laser.



Figure 11. Pulsed laser light entering the mini-chamber

CHAPTER IV

EXPERIMENTAL RESULTS

Preliminary testing

Before the laser experiment could be conducted, preliminary testing of the sample and setup had to be done to ensure the device was working properly under the principles of field emission and followed the slope of Fowler-Nordheim tunneling. The diamond coated silicon and the bare silicon were each tested. From the Fowler-Nordheim equation, if 1/F is plotted against $\ln(I/V^2)$ there should be a negative linear slope to show field emission. A plot of each F-N curve is shown in figure 12. It should be noted that a range of potential from 3000 V to 5000 V was used to construct the plot. The emission was on the order of nanoamps and emission at potential lower than 3000 V could not be separated from noise. Figure 13 shows both the diamond coated silicon and the bare silicon with a negative linear slope, so regular field emission can be assumed. After the preliminary testing of emission was successful, the experiment was then moved to the laser testing lab where thermionic emission and the Schottky effect could be observed.

Field Emission I-V



Figure 12. Field Emission I-V Characteristic

Fowler Nordheim Emission



Figure 13. Fowler-Nordheim plot. Units of current are in nA, while units of F are in $V/\mu m$

Schottky Effect

First, emission of pure silicon was tested using the laser as a heat source. The laser energy was measured to be 320 mV using a multimeter. To convert this into Wm^{-2} the measured potential was divided by 87 mV W^{-1} to get the power in Watts, which was then divided by the frequency of the laser pulse, 10 Hz, to give joules per pulse. This was then divided by the length of a pulse, 10 nanoseconds, and then finally divided by the area of the beam, which had a radius of 4 mm. The laser energy was calculated to be 7.31 x $10^{11} Wm^{-2}$, and it was at this energy level that the Schottky curve was constructed. To plot each point, the voltage was increased in increments of 100 V. At each input (100 V, 200 V, etc.) five measurements were made of the output by using an oscilloscope to measure the voltage across the resistor. An average of the five outputs was used as the final output value.

After performing the experiment on the bare silicon sample, the process was repeated for the diamond coated silicon device. The laser energy was measured at 230 mV and calculated to be 5.26×10^{11} Wm⁻². Figure 14 shows a plot of the data from both the silicon and silicon-on diamond diodes fitted to a Schottky curve while figure 15 shows sample oscilloscope measurements taken from each device at different input voltages. From the plots we can see that the natural log of current versus the square root of voltage shows a linear curve with R² values of .9862 and .9853 for silicon and diamond respectively. These are characteristics of Schottky emission[22], and therefore are currents that depend on temperature and electric field. The value of the currents in each plot cannot be compared to each other or any future current measurements in this experiment because the vacuum distance between anode and cathode is changed; the electric field is altered, so the only conclusion made from these plots is the linearity shows Schottky emission.



Figure 14. I-V curve for each device



Figure 15. Plot of natural log of current versus square root of voltage (Schottky)

<u>Current – Temperature Relationship</u>

Current emission was recorded at varying levels of laser energy, ranging from 3.06×10^{11} Wm⁻² to 1.2×10^{12} Wm⁻² for both the silicon and silicon on diamond samples. Input voltage was fixed at 40 V for the silicon and 300 V for the diamond on silicon. The measured laser energy was converted to temperature using a numerical simulation of the heat transfer equation using Mathematica. Comparisons of the two samples are shown in the plots below. Figure 16 shows the raw data collected, a plot of current versus silicon lattice temperature. Figure 17a is an Arrhenius plot of the natural log of the current divided by the temperature squared versus the inverse of temperature using parameters of the material at 300 K while figure 17b shows the same plot using parameters at 1400 K. Two different plots are necessary because two of the constants used in the simulation, thermal diffusivity and thermal conductivity, vary with temperature. These figures come from a derivation of Richardson's equation, where the slope of the Arrhenius plot gives the negative of the activation energy, which in this case is the energy required for an electron to emit from the surface of the diamond or silicon cathode.



Figure 16. A plot showing the raw data of current versus lattice temperature



Figure 17 a) Arrhenius Plot of temperature versus current using 300 K parameters and b)using 1400 K parameters

The linear slope of the Arrhenius plot can be used to solve for the activation energy needed for electrons to emit based on Richardson's equation:

$$I = AT^2 \exp\left(\frac{-\phi}{kT}\right) (10)$$

Converting this into an Arrhenius equation yields:

$$\ln\left(\frac{I}{AT^2}\right) = -\left(\frac{\phi}{kT}\right) (11)$$

meaning that the Arrhenius slope found in figure 17b is the negative of the activation energy divided by the Boltzmann constant, 8.617×10^{-5} eV K⁻¹. Multiplying the slope by *k* yields activation energy of 0.594 for the silicon sample. The diamond sample shows two distinct slopes, so the slope has been calculated twice for the two regions of the diamond curve. The first slope, seen at lower temperatures, has activation energy of 0.587 eV. This is very similar to the activation energy seen in the silicon. A secondary slope shows activation energy of 0.02 eV at higher temperatures in the diamond sample.

The work function of silicon is 4.5 eV, but the activation energy found from the slope of figure 17b is approximately 0.6 eV. In order to compensate for this discrepancy, an adjusted Arrhenius plot was made by increasing the temperature by a factor to show the proper known work function. The adjusted plot is shown in figure 18. The adjusted temperature is the electron temperature, while the unadjusted temperature was the simulated lattice temperature of the surface of the silicon.



Figure 18. Adjusted Arrhenius plot

The adjusted plot shows a dramatic shift in slope for the diamond on silicon device occurring at electron energy of 1.7 eV. This value was expected to be the electron affinity of silicon, 4.05 eV, the distance between the conduction band the vacuum energy level. The discrepancy means that at a level of 1.7 eV above the Fermi level of silicon, electrons were able to enter the band gap of diamond and emit. In order to reach the vacuum level, trapped energy states in the diamond were released in a stair-like fashion until the energized electron reached the conduction band of diamond. At this point the silicon on diamond begins to show the work function of diamond. According to the slope of the silicon on diamond at high temperature the work function is 0.2 eV, much closer to that of diamond than silicon. Although the exact number is unknown, diamond has work function close to 0 eV and negative, meaning the vacuum level of diamond will be nearly identical to its conduction

band. At this junction, electrons can be inserted directly into the conduction band of diamond. Due to the small and negative electron affinity of diamond, emission is highly efficient if its large band gap, 5.5 eV, can be overcome. As shown from the adjusted Arrhenius plot, electrons energized at over 1.7 eV can emit from the diamond surface to the vacuum energy level.

Conversion Efficiency

Conversion efficiency is calculated by taking the power of the input and dividing by the energy of the output. A sample input energy for diamond is .264 Joules/pulse, which comes from the 230 mV measured laser energy used in the experiment. The output energy of this system can be calculated by squaring the output current (.01 A) and multiplying by resistance (500 Ω) to give power. Multiplying by the pulse width (10 ns) will give Joules/pulse. This number comes out to 5 x 10⁻¹⁰Joules/pulse. Dividing the output by the input gives a small ratio of 1.89 x 10⁻⁹, which is the energy conversion efficiency for this system.

The small conversion efficiency can be attributed to the small surface area where the emission occurred compared to a large surface area of the laser. The laser light hit a large part of the vacuum chamber, estimated at a diameter of approximately one inch. The point at which emission occurred was much smaller than this, on the order of several micrometers. Lens absorption and refraction also could have caused loss of energy. The energy used to pass through the glass window and the way the laser light bounced off the glass and other parts inside of the vacuum chamber contributed to lower conversion efficiency. Also, impurities due to handling of the substance likely caused efficiency to drop. During experimentation the observed output voltage would often need to stabilize until it reached a

constant value. This was due to the laser burning off impurities present on the sample, since the impurities make an undesirable added path for heat transfer. The power required to heat the sample used comparatively high levels of energy while the emission caused by the laser had much lower energy.

Ionization Effects

The ionization effects pertain to the release of electrons due to plasma effects as the air surrounding the material can become ionized. Plasma is an ionized gas that has a sufficient amount of free charge to be significant [24]. Under negative bias when no output of current or potential was expected, the oscilloscope still displayed some amount of noise. This can be attributed to ionization effects as the chamber was not under true vacuum conditions but was very close with a very low pressure of 10^{-4} torr. This effect can be seen in the oscilloscope readings found in the appendix.

CHAPTER V

CONCLUSION

Under vacuum conditions and subjected to high voltage levels, the bare silicon and diamond coated silicon samples showed Fowler-Nordheim field emission, ensuring that each vacuum device was working properly. When exposed to the 532 nm Nd:YAG laser to increase the temperature, each device showed Schottky emission. Finally, an Arrhenius plot was made to show the effects of thermionic emission by Richardson's equation by increasing the laser energy, thereby increasing the electron temperature. After adjusting the plot to reflect the known work function of silicon, the transition point from silicon emission to diamond emission was found.

The activation energy obtained from the results of the adjusted Arrhenius plot suggests diamond begins to emit at electron energy 1.7 eV above the conduction band of silicon. It was hypothesized that the transition point would be 4.05 eV, the electron affinity of the silicon sample and also the energy above the conduction band of silicon required to reach the conduction band of diamond. The electron energy of 1.7 eV corresponds to a level short of the vacuum energy level. It is concluded there are trapped energy states within the diamond that allow electrons to make a jump from this electron energy level to the conduction band of diamond. It was at this energy level that the emission began to show a work function close to zero as seen from the slope, showing the transition from silicon emission to diamond emission. Since diamond has a low work function, if electrons can be inserted into the conduction band, further energy will not be needed to reach the vacuum level, thereby making emission highly efficient. It is recommended that further tests be done

to further explain the mechanism in which the electrons inserted into the band gap of diamond make their way to the conduction band.

The system for achieving thermionic emission of diamond had a low energy conversion efficiency, 1.89×10^{-9} . Comparatively high input laser energy, nearly 10 orders of magnitude greater, was required to produce thermionic electron emission. This was due to several factors including impurities in the sample, the distance electrons had to travel to contribute to emission, and the laser hitting a larger area than necessary and also being partially reflected by the surface of the silicon. It is recommended that further study be done to relate the efficiency of the system to its effectiveness in other applications.

REFERENCES

- [1] A. Van Der Ziel, *Solid State Physical Electronics Third Edition*, Prentice Hall, Englewood Cliffs, New Jersey, 1976.
- [2]. O. W. Richardson, "Thermionic phenomena and the laws which govern them," *Nobel Lecture*, December 12, 1929.
- [3] R. S. Muller and T. I. Kamins, *Device Electronics for Integrated Circuits Third Edition*, John Wiley and Sons, Inc, 2003, Chapter 3.
- [4] S. M. Sze, *Physics of Semiconductor Devices, Second Edition*, Wiley and Sons, Inc, 1981, Chapter 5.
- [5] Y. Khlifi et al., "Modeling of Fowler-Nordheim current of metal/ ultra-thin oxide/ semiconductor structures," *M.J. Condensed Matter* Vol. 3, No. 1, 53-57, July 2000.
- [6] D. Saada, "Ion Implantation into Diamond and the Subsequent Graphitization" (PhD Dissertation, Technion: Israel Institution of Technology, 2000).
- [7] Synthetic Diamond Emerging CVD Science and Technology', Spear and Dismukes, Wiley, NY, 1994
- [8] G.V. Samsonov (Ed.) in *Handbook of the physicochemical properties of the elements*, IFI-Plenum, New York, USA, 1968.
- [9] R. Hull, *Properties of Crystalline Silicon*, London: The Institute of Electrical Engineers, 1999.
- [10] R.F. Pierret, *Semiconductor Device Fundamentals*, Prentice Hall, November 2, 1995.
- [11] G.W.C. Kaye and T.H. Laby in *Tables of physical and chemical constants*, Longman, London, UK, 15th edition, 1993.
- [12] R. D. Knight, *Physics for Scientists and Engineers: A Strategic Approach*, Pearson Education, 2004.
- [13] A. Marcus and J. R. Thrower, *Introduction to Applied Physics, Second Edition,* Breton Publishers, 1985, Chapter 13.
- [14] R. Paschotta, "Intensive light pulses, tailored to your needs", *Laser+Photonik* May 2005.
- [15] D.J Goldberg and J.A. Samady, "Evaluation of a long-pulse Q-switched Nd:YAG laser for hair removal". *Dermatologic Surgery* 2000 Feb;26(2):109-13.

- [16] M. K. Loze and C. D. Wright, "Temperature distributions in laser-heated biological tissue with application to birthmark removal," *Journal of Biomedical Optics* 6, Vol. 1, 74-85, January 2001.
- [17] M. Kaylon and B. S. Yilbas, "Analytical solution for laser evaporative heating process: time exponentially decaying pulse case," *Journal of Physics D: Applied Physics* 34, 3303-3311, 2001.
- [18] B.S.Yilbas and M. Sami, "Heat transfer analysis of semi-infinite by a laser beam," *Heat and Mass Transfer* 32, 1997.
- [19] P. Okon et al, "Laser Welding of Aluminum Alloy 5803," 21st International Congress on Applications of Lasers and Electro-Optics, Scottsdale, October 14-17, 2002.
- [20] M. Salib et al, "Silicon Photonics," *Intel Technology Journal*, Vol. 8, No. 2, May 2004.
- [21] www.coherent.com
- [22] P.W. May et al, "Field emission mechanisms in chemical vapor deposited diamond and diamondlike carbon films," *Applied Physics Letters* Vol. 72, No. 17, 2182-2184, April 1998.
- [23] W.H. Hayt, J.E. Kemmerly, and S.M. Durbi, *Engineering Circuit Analysis*, 6th edition, McGraw-Hill, 2002.
- [24] H. R. Griem, *Principles of Plasma Spectroscopy*. New York: Cambridge University Press, 1998.

APPENDIX

Mathematica Source Code for 3D Conduction Limited Case (constant laser)

To create the temperate versus time and distance and temperature versus distance plots, a Mathematica notebook was created to run the heat transfer equation. The first case is a constant laser and the second case is a pulsed laser.

Laser Energy 3. x 10¹¹ Wm⁻² Input Code (Constant Laser case)

 $\gamma = 3.06 * 10^{11}$ (* laser peak power intensity available at the surface Wm⁻² *); k = 156 (* thermal conductivity Wm⁻¹ K⁻¹ *); $\delta = 6.8 * 10^5$ (* absorption coefficient m⁻¹ *); $\alpha = 8.6 * 10^{-5}$ (* thermal diffusivity *);

 $\operatorname{ierfc}[x_] := 1/\operatorname{Sqrt}[\pi] * \operatorname{Exp}[-x^2] - x * \operatorname{Erfc}[x];$

(*Analytical Solution without time dependecy*)

$$\begin{split} temp[x_,t_] &:= (2*\gamma)/k * Sqrt[\alpha*t] * ierfc[x/(2*Sqrt[\alpha*t]] - \gamma/(k*\delta) * Exp[-\delta*x] + \\ \gamma/(2*k*\delta) * Exp[\alpha*\delta^{2}*t-\delta*x] * Erfc[\delta*Sqrt[\alpha*t] - x/(2*Sqrt[\alpha*t]] + \\ \gamma/(2*k*\delta) * Exp[\alpha*\delta^{2}*t+\delta*x] * Erfc[\delta*Sqrt[\alpha*t] + x/(2*Sqrt[\alpha*t]]; \end{split}$$

f = FullSimplify[$\partial_t \text{temp}[x,t]/\alpha$] - $\partial_{x,x}\text{temp}[x,t]$];

Plot3D[f,{x,0,10*10^-6},{t,10^-9,10^-8}]



Plot3D[temp[x,t],{x,0,10*10^-6},{t,10^-9,10^-8}]



Laser Energy 3.64 x 10¹¹ Wm⁻² Input Code (Pulsed Laser case)

(*Time dependent heat source*)

 $[t_]:=(1-Exp[-(t)/\tau])/;t < td$

 λ [t_]:= (1-Exp[-t/ τ])- (1-Exp[-(t-td)/ τ])/;t≥td

 $td=10^{-8}; \tau=10^{-8};$ $Plot[{\lambda[t]}, {t,0,10^{-7}}]$



NIntegrate[λ [t],{t,0,10^-8}]+NIntegrate[λ [t],{t,10^-8,10^-5}]

(*Numerical solution of time dependent heat pulse*)

solution = t
u/. First [NDSolve[{
$$\partial_t u[x,t]/\alpha - \partial_{x,x} u[x,t] = = (\gamma^* \delta/k) * \text{Exp} [-\delta^*x] * 2 * \lambda [t]$$

 $u[x,0] = = 0, u^{(1,0)}[0,t] = = 0, u[0.01,t] = = 0$ }, u, {x,0,0.01},
{t, 0, 10^-6},
Method \rightarrow {"MethodofLines", "SpatialDiscretization" \rightarrow
{"TensorProductGrid", MinPoints \rightarrow 25000}}]];

 $Plot3D[solution[x,t], \{x,0,10^{-5}\}, \{t,10^{-9},10^{-7}\}, PlotRange \rightarrow All, PlotPoints \rightarrow 25]$



Plot[solution[10^-6,t],{t,10^-8,10^-7}]



Sample Oscilloscope measurements

Oscilloscope measurements for Silicon at a) -500 V and b) -1000 V and Diamond at c) -500 V and d) -1000 V. The silicon laser energy was 7.31×10^{11} W m⁻² while the diamond coated silicon laser energy 5.26×10^{11} W m⁻². The top curve in each screenshot is the voltage measured across the resistor, and the bottom curve shows the laser pulse. This is to show that the voltage pulse is in synch with the laser. The scale is indicative of the measured voltage and not the laser pulse.

