Understanding Lifetime Dynamics in Gold Hyperdoped Silicon Solar Cells

by

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Abstract

Silicon is a commercially predominant solar cell material used in the study of hyperdoping, in which an element is added to broaden the range of light captured by the cell. The electrons in the hyperdoped silicon are excited by sending ultra-fast pulsed light through the sample and their conductivity is measured by a function of time. That conductivity decay rate is a measure of how fast the electrons are relaxing i.e. carrier lifetime. However, particular samples produce a bi-exponential decay curve with two different lifetimes as fast and slow decay. We hypothesized that the fast and slow decay stem from an uneven distribution of dopant concentration across the depth of the cell that is created by the manufacturing process of hyperdoped silicon. The silicon crystalline structure is melted to add in the dopant and then a super-cooling process re-solidifies the material. The speed of cooling affects the amount of dopant accepted into the silicon structure, subsequently causing a pile-up of dopant near the surface of the cell. We show with experimental that the fast decay correlates to a higher concentration profile by exciting at different depths where the concentration of gold dopant varies. The correlation is further proved with a numerical simulation of the fast decay based on diffusion of carriers and a depth-dependent recombination rate. Through experiment and numerical modeling, we hope to better our ability to increase cell efficiency through different doping techniques.
Dedication

To my 9th grade Physics teacher who introduced me to all the amazing things in this world and the tools for making sense of it all.
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Chapter 1

Introduction

1.1 Solar Energy

The research surrounding renewable energy technology has been present for years, but the growing conversation regarding the need for efficient technologies to replace our fossil fuel consumption and save the future of our environment is rapidly inspiring many to find ways to live a greener life. One path is through solar photovoltaics (PV). Research behind solar energy is important, because a more efficient PV panel can reduce the initial investment cost of materials as well as the land area needed to generate the same amount of electricity. Recent cost comparisons for solar projects on the scale of megawatts report a price drop of 0.36 to 0.10 USD per kwh between 2010 and 2017 compared to 0.07 USD per kwh for fossil fuels [1]. This price will continue to drop either from one, increasing the efficiency of particular PV modules, or two, lowering the material costs.

1.2 Silicon Photovoltaic

Silicon is a commercially predominant material already widely used in the PV world. Bulk silicon makes up roughly 94% of the solar cell market as of 2006 [2]. Bulk silicon panels, however, are very expensive due to the need for thick cuts of ultra-
pure silicon (~ 200 µm). For this reason, there is promise in thin-film technologies that can be as thin as a few micrometer. They are also more flexible and lighter in weight; however, thin film technology still struggles to compete with conventional silicon on the market. For solar cell materials, there is a range of developmental stages from simply theoretical to commercial. The goal is to move a material up this ‘scale’ by refining and perfecting the technology through repeated experimentation and analysis. Each year, the National Renewable Energy Laboratory updates a graph of the highest efficiencies for various photovoltaic technologies that have been experimentally confirmed by accredited laboratories, dating from 1976 to current [3]. For thin film materials, the highest efficiency achieved to date is roughly 23% as can be seen in Figure 1.1.

Figure 1.1: Record solar cell efficiency by technology over the years. Figure adapted from Ref. [3].
The efficiency of a solar cell may be simply defined as the power output over the power input. In other words, we want to convert as much of the incoming light into electricity as possible. There are many loss mechanisms such as thermalization, extraction, and transmission identified in Figure 1.2. Thus, for a single solar absorber only 33% of the solar radiation could theoretically be captured. This is called the Shockley-Queisser efficiency limit for a single p-n junction solar cell, which is shown in the inset of Figure 1.2 [4]. Multiple high efficiency concepts have been proposed to diminish these losses and push efficiency limits [5]. Among which, there is theoretical work showing that efficiencies greater than 50% are possible for intermediate band photovoltaics [6].

Figure 1.2: Solar Spectrum with color-coded energy loss analysis in a silicon solar cell adapted from Ref. [7]. Inset: The Shockley-Queisser efficiency limit as a function of semiconductor energy band gap. Figure adapted from Ref. [4].
Characterization of materials in the developmental phase is vital to identifying the most valuable parameters to capturing as much of incoming sunlight as possible. In order to convert sunlight to electricity, the incoming rays must have an energy equal to or larger than the band gap energy of the semiconductor in order to excite the electrons from the valence band to the conduction band (Figure 1.3). This band gap energy varies depending on the material. Once the electron is excited to the conduction band, the energy extraction depends on how quickly the electron is transported out (mobility of the electron) and how quickly the electron relaxes its energy. The process of an electron relaxing back down is called recombination. A faster recombination rate minimizes the length of time the electrons spend in the conduction band, thus reducing the total energy available for conversion. This length of time between excitation and recombination is referred to as lifetime and will be the key parameter of characterization in later chapters.
1.3 Intermediate Band Photovoltaic (IBPV) and Hyperdoping

Intermediate band photovoltaics (IBPV) is promising for exceeding the Shockley-Queisser efficiency. The setup of the IBPV is the same as in Figure 1.3, but with an intermediate band added in between the valence and conduction band (Figure 1.4). Now photons with energy smaller than the bandgap can be utilized by a two-step conversion process: two low energy photons first excite an electron from the valence band to the intermediate band, and then from there to the conduction band. This creates one high-voltage electron-hole pair and at the same time a larger portion of the solar spectrum is absorbed. This has been noted in studies of increased absorption of light from adding an intermediate band. Measurements of the absorption
coefficient of a IBPV material show increased absorptance at a larger range of wavelength i.e. smaller energies (Figure 1.4) [8].

One way to engineer the intermediate band is through a process called hyperdoping, in which high concentrations of an element like sulfur are added to silicon. In addition to sulfur, different elements in the periodic table have been investigated for intermediate band formation. Among transition metals, gold and zinc are the two most promising elements reported [9]. The introduction of these elements into silicon is a delicate process, highly sensitive to any variability in manufacturing parameters.

The hyperdoping process is a three-step process shown in Figure 1.5 [10]. The first step being ion implantation, where high concentrations of dopants, concentrations above thermodynamically achievable, can be incorporated into a host material. The high concentrations of dopant are bombarded into crystalline silicon through ion
implantation, leaving damaged amorphous silicon. To reverse this damage, the material is then melted into a molten liquid through a series of laser pulses (pulsed laser melting; PLM). The laser melting process provides a fast cooling and rapid solidification time scale. In this process, the damaged silicon recrystallizes while the dopants are trapped in the host lattice at ultrahigh concentrations. However, the speed of cooling has large effects on the final outcome and there is always a chance for the structure to not properly recrystallize, leaving defective regions in the crystal arrangement.

Figure 1.5: (a) Schematic of the steps in dopant incorporation into silicon from ion implantation to PLM to rapid solidification and (b) the subsequent concentration profile of gold dopant across the depth of the material. Figures adapted from Ref. [11].

The rapid solidification process has been of great interest to experimenters working with hyperdoped silicon. The speed of solidification is defined as the interface velocity between the liquid and solid regions of the material during cooling. The
interface velocity must be faster than the diffusive speed of the dopant in silicon so as to capture as much of the element before it is pushed out. On the other hand, the re-solidification must be slow enough so instability at the solid-liquid interface does not develop (too fast and the result would be an amorphous lattice). Thus, many hyperdoped materials can be uniquely identified by a characteristic pile-up of dopant at the surface of the material caused by this process (Figure 1.5.b), which will be the focus of this thesis.

The “Continuous Growth Model (CGM) for interface motion during alloy solidification” is a model that predicts how much dopant is trapped in the laser melting process. The partition coefficient $k$ is defined as the concentration of dopant in the solid phase over the concentration of dopant in the liquid phase at the solid-liquid interface as the material is re-solidifying [12]. The model predicts the percentage of dopant concentration pushed out across the depth of the material during the cooling process as:

$$k(v) = \frac{k_e + \frac{v}{v_D}}{1 + \frac{v}{v_D}}$$

(1.1)

The partition coefficient, $k$, is determined by the velocity of cooling ($v$) and the velocity of diffusion ($v_D$) of the dopant element of choice, and $k_e$ is the equilibrium partition coefficient. In Equation 1.1, the fraction $v/v_D$ helps to numerically explain the aforementioned phenomena that a slower cooling velocity will allow time for the
silicon to push the dopant element out. In other words, as the cooling process moves across the depth of the sample from the back to the surface, there is an increasing accumulation of gold being pushed forward. The slower the cooling speed is, the more the diffusive speed of the dopant in silicon in that denominator wins out. Figure 1.6 displays visually how the dopant concentration varies depending on the calculated \( k \), and thus the cooling velocity using Equation 1.1. Figure 1.6 depicts how a slower cooling velocity will cause a smaller partition coefficient, in which a smaller percentage of gold will be incorporated evenly. And thus we are left with a larger percentage of the initial concentration piled up near the surface of the sample.

![Graph](image)

Figure 1.6: The concentration profile for arsenic (As) in silicon with different cooling rates. The figure compares the surface pile-up of dopant and the calculated partition coefficient. The slower the cooling rate, the higher the pile-up of As concentration near the surface. Figure adapted from Ref. [13].
Comparing various doping elements in silicon, Ref. [9] singled out gold and zinc, because they were best at being incorporated into silicon at the highest concentrations without cellular breakdown. This has to do with the behavior of gold and zinc in silicon and their diffusive speeds within silicon. In further experiments run in our own lab comparing lifetime, gold stood out against zinc as having a long lifetime. In Ch.2, the process for measuring lifetime in experiment will be explained.

1.4 Conclusion

The goal of this thesis is to identify the interplay between dopant concentration profile created by different PLM process parameters and the charge carrier lifetime of the material through both experiment and modeling. In this chapter, the workings of a semiconductor were laid out to introduce the intermediate band created through hyperdoping silicon with an element, which is gold for this thesis. The sensitive nature of the PLM process produces this characteristic concentration profile that is studied. Ch.2 and Ch.3 of this thesis focus on experimentally determining carrier lifetime, while Ch.4 introduces the simulation that was created to model our experimental data. Lastly, Ch.5 presents the results and discussion of the simulation in regards to both experiment and predictive work.
Chapter 2

Ion Implantation Energy

2.1 Introduction

The process of pulsed laser melting and its effects on the characteristic concentration profile of hyperdoped silicon was discussed in the Introduction. In this chapter, the effects of ion implantation energy will be analyzed by comparing the measured lifetime of 3 samples that differ only in the energy used to implant the gold. By comparing implantation energies of 50, 110, and 300 keV, respectively, we hope to understand how the energy at which the dopant is implanted affects the lifetime of the sample. Moreover, we are looking for comparisons between the different distributions of gold across the depth of the sample, i.e. the concentration profile and the corresponding lifetime measurement for each sample.

The conductivity of a semiconductor is equal to the product of the charge, the velocity at which the electrons move through the sample, and the density of electrons. The more gold atoms we are able to implant i.e. the higher concentration of gold, the more photons we may absorb. This has to do with the similar discussion in the Introduction (Figure 1.4); an intermediate band allows for a larger range of wavelength to be absorbed. This is experimentally shown in Figure 2.1 with higher
absorptance at higher dopant concentrations. Returning to the initial statement regarding the conductivity of the material, the more photons we are capable of absorbing, the higher the density of electrons in the conduction band and thus the more conductive our material is.

![Graph showing absorptance with increasing Au dopant dose and sub-band gap absorptance.](image)

Figure 2.1: Comparison between increasing Au dopant dose and sub-band gap absorptance. Figure adapted from Ref. [11].

In addition to conductivity, however, the recombination rate also increases with higher concentrations of gold. An increase in dopant concentration subsequently increases the density of intermediate states. This may be thought of as thickening or saturating the intermediate band. Although an increase in the sites where an electron may ‘jump up’ benefits the conductivity of our material, these sites may also be
thought of as paths for recombination. Thus, the more sites for recombination, the 
fastier our electrons relax back down. This decreases our lifetime, which is why 
lifetime measurements are so important to identifying promising material parameters.

2.2 Lifetime and Gold Concentration Profile

“Lifetime metrology can be used to assess the impact of materials processing more 
quickly and with greater accuracy than the fabrication and test of complete solar cell 
devices” [14]. The difference between the experimental phase and commercial phase 
was described in the introduction. In research, this difference is made clear by 
distinguishing an absorber material from a device. Before we can start working on 
devices, it is important to check all the boxes indicative of a good absorber material 
for a solar device: band gaps, absorptivity, lifetime, and mobility [15]. These 
parameters may be used to create a sort of standard of comparison between samples 
called a figure of merit (FOM) that is defined in Equation 2.1.

\[
FOM = \frac{E_g}{q} \mu \alpha^2 \tau
\]  

(2.1)

In Equation 2.1, \(E_g\) is the band gap energy (1.1 eV for silicon), \(q\) is the elementary 
charge, \(\mu\), \(\alpha\), and \(\tau\) are the mobility, absorption coefficient, and lifetime, respectively. 
The mobility is taken from literature values for gold in silicon. From the 
aforementioned data on absorptivity in Figure 2.1, we choose to use a dose of \(10^{15}\)
gold atoms per square centimeter for our later experiments. From now on, this thesis will focus solely on the lifetime parameter in comparing our samples.

To return to the initial discussion of this chapter, the implantation energy now becomes of importance as we begin to study the effect of the distribution of gold concentration across the depth of the material. As the implantation energy is increased, the penetration depth increases. The concentration of gold is now spread deeper into the material, which means that there is a larger amorphous region. The PLM process is the same for these three samples; however, it takes less energy to melt an amorphous region than a crystalized region. Thus, the outcome of the PLM process may vary across the three samples, which will most likely cause differences between the concentration profiles of each. Acknowledging this, we sent out samples for secondary ion mass spectrometry (SIMS) at EAG Laboratories (EAG.com) for concentration profiling.

Figure 2.2 plots the resulting profile for the concentration of gold across depth for each sample of different implantation energy. The surface (depth = 0 nm) region of the sample depicts a trend of increasing concentration of gold dopant with decreasing implantation energy. The sample implanted at 50 keV has the highest surface pile-up. However, it should be noted that between 50 and 100 nm, this trend switches. The concentration of gold is now higher at a higher implantation energy. This particular trend is emphasized in the inset plot of Figure 2.2 that graphs the concentration
profile on a log plot. The area under the curves are the same for these three samples, corresponding to the gold dose of $10^{15}$ cm$^2$. The analysis of these trends will be important later in the discussion of experimental results.

![Au Concentration Profile](image)

Figure 2.2: SIMS Data showing the relation between concentration profile across depth and increasing implantation energy from 50 to 110 to 300 keV. Inset: Log plot of concentration across depth.

2.3 Pump Probe Measurements

We use terahertz (THz) spectroscopy to perform lifetime measurements of these three samples in the lab (Figure 2.3). Firstly, spectroscopy may be simply defined as the study of absorption and emission of light by matter. In our experiment, we want to identify the number of free carriers, or electrons, that are in the conduction band at
any point in time. Free carriers absorb THz, so we can monitor the absorption of THz. To do this, we measure the amount of THz that is transmitted and then subtract that from the initial incoming THz to solve for the THz absorbed by the sample. The time component is created by using a delay stage. A delay stage is two mirrors on a moving stage where light goes in to one mirror and gets reflected onto the second and sent back the same way. This allows us to modify the path length of the light. Ultrafast pulsed light at a wavelength of 400 nm is used as the excitation light and is setup with the delay stage so as to vary the arrival time of the excitation pulse to the sample. Each specified step along the delay stage corresponds to a data measurement of THz through the sample. When the excitation pulse arrives at the same time as the THz, we observe the maximum THz reduction since most charge carriers are present to attenuate the THz pulse. As the delay stage moves, the excitation pulse (pump) arrives earlier than the THz probe pulse. Within the pump-probe time difference some carriers recombine so as the delay stage moves, the reduction of THz signal decreases.
This THz signal is plotted as a function of the delay stage position (Figure 2.4.A) and this decay is proportional to the conductivity decay rate, which is a measure of the lifetime. The analysis is carried out in Mathematica to plot each consecutive step in the process of converting the THz signal in volts vs. delay stage position to a normalized change in conductivity vs. time in picoseconds that can then be fitted to identify a numerical value for the lifetime of the material. First, the initial raw data must be manipulated so that the peak lines up with time zero, the time at which the excitation pulse and THz signal arrive simultaneously. Then the x-axis is converted from position in mm to time in picoseconds (Figure 2.4.B) by a simple calculation. For every 1 mm the delay stage moves, the path of light increases by 2 mm (1 mm out
and 1 mm back). We calculate 1 mm movement in delay stage position to be equivalent to a timestep of about 7 picoseconds.

\[ \Delta t = \frac{2\Delta x}{c} = \frac{2(1 \times 10^{-3} m)}{c} = 6.67 \text{ ps} \]  

(2.2)

Next, we must find the amount of light absorbed by taking the difference between the transmitted and initial light, symbolized as a change in THz signal in Equation 2.3.

\[ dT = T_{with\ pump\ on} - T_{with\ pump\ off} \]  

(2.3)

We must then normalize this voltage signal to the base signal that is transmitted when there is no excitation pulse going through the sample. This is done using an average, \( T_0 \), of 100 data points taken when just THz pulse is running through the sample without pump excitation (Figure 2.4.C). Lastly, we normalize our plot again to one by dividing by the max signal, \( dT_{max} \), at time zero. Additionally, we make the signal positive for ease of viewing and analysis later (Figure 2.4.D).
The experimental plots, outlining the consecutive steps from the change in THz transmission across delay stage depth to a normalized decay over time.

The last step before fitting is to convert this now to change in conductivity (\(\sigma\)), which is proportional to the change in THz transmission calculated in Equation 2.3. The change in conductivity is calculated in Equation 2.4, where \(n\) is the index of refraction, \(z_o\) is the impedance of vacuum, 377 \(\Omega\), equivalent to \(\sqrt{\mu_0/\varepsilon_0}\), and \(d\) is the depth of absorption equivalent to \(1/\alpha\). The change in conductivity is graphed in Figure 2.5.

\[
\Delta \sigma = \sigma_{\text{pump on}} - \sigma_{\text{pump off}} = \frac{n_{\text{air}} + n_{\text{Si}}}{z_0 d} \left( \frac{-\Delta T}{T_o} \right)
\]  

(2.4)
Figure 2.5 The normalized change in conductivity over time. Inset: Figure plotted on a log scale.

2.4 Data Analysis and Fitting Process

Eventually, we reach the fitting process. We want to know how many carriers remain in the conduction band over time. In other words, the rate of change in conductivity over time. If you think about what is occurring in the conduction band, the number of excited carriers decays when more electrons are recombining than are excited. The rate of decay increases when the recombination rate increases, which may also be described in terms of a shorter lifetime for excited carriers. This translates to an inverse relationship between lifetime (τ) and the number of carriers (n) in the conduction band over time (Equation 2.5).
\[ \frac{dn}{dt} = -\frac{n}{\tau} \] (2.5)

The larger or steeper the decay in Figure 2.5, the shorter the lifetime. Whereas, the smaller the decay, the longer the lifetime. In our analysis we first look at fitting an exponential to the conductivity decay rate. Solving for Equation 2.5, we get Equation 2.6.

\[ \frac{n(t)}{n(t = 0)} = e^{-t/\tau} \] (2.6)

In the fitting process for the three samples, we notice that the decay rate is not actually a single exponential. Referring back to Figure 2.5, the change in conductivity over time has a noticeable difference between the rate of decay in roughly the first 25 picoseconds compared to the rest. This is further proven in the inset log plot depicting a non-linear trend in the data. Therefore, the data is better fitted to the bi-exponential with two lifetimes (\(\tau_{fast}\) and \(\tau_{slow}\)) with different weights \(a_1\) and \(a_2\) \((a_1 + a_2 = 1)\), in Equation 2.7.

\[ \frac{n(t)}{n(t = 0)} = a_1 e^{-t/\tau_{fast}} + a_2 e^{-t/\tau_{slow}} \] (2.7)
Analyzing lifetime dynamics is important to identifying a good absorber material for solar devices; however, how do we know what lifetime really means if we have two different lifetimes that we are comparing? Which one is more significant to our comparison between implantation energies? Since observing this bi-exponential decay, we have chosen to emphasize the fast lifetime in comparing materials. Based on this decision, we compare the fast lifetimes of the three samples at differing implantation energy in Figure 2.6.

![Normalized Change in Conductivity](image)

**Figure 2.6:** Comparison of the normalized change in conductivity over time for the three samples of differing implantation energies. Inset table provides the fitted fast lifetimes for each sample.

We see that the fast lifetime value is greatest for the lower two of the three implantation energies, being 50 keV and 110 keV, but seems to decrease significantly
for the 300 keV sample. From this fit, we may say there is an inverse relationship between implantation energy and lifetime. If we think about how implantation energy affects our samples: the deeper that the gold penetrates, the deeper the damaged area is that PLM and rapid solidification must attempt to recrystallize properly. This may simply be explained by the fact that a higher implantation energy is slamming gold ions into the silicon at a higher intensity. Think of the gold dopant as a tennis ball and now think of the difference in damage created by a pro tennis player verses a child hitting that tennis ball. Thus higher implantation energies can subsequently create defects affecting lifetime dynamics. The very short lifetime we see at a high implantation energy makes sense with this logic.

However, if we compare these lifetime results with the concentration profiles plotted in Figure 2.2, it identifies a faster lifetime with a lower surface pile-up of gold. Although, remember that the concentration of gold was higher for the 300 keV sample if we focused on the middle of the sample. This was made clearer by plotting the gold concentration on a log plot in the inset graph of Figure 2.2. This perspective now identifies a different trend in which a faster lifetime corresponds to a higher pile-up of gold. These results lead to a question about the depth at which our experiment is probing.
2.5 Conclusion

The comparison between implantation energies, relying heavily on theory to spot trends between the fast lifetime and the surface pile-up of gold dopant, led to an interesting question. What part of the concentration profile are we probing? In addition to the question of excitation depth, there is still the remaining issue of understanding why the decay fit is bi-exponential. It is possible that the explanation to both of these questions lies in the depth-dependent concentration profile of gold in the samples. In Ch.3, an experiment is built to vary the probe depth of excitation so that data may be collected when probing a sample at a higher verse lower dopant concentration region.
Chapter 3

400 nm vs. 266 nm Experiment

3.1 Introduction

In the previous chapter comparing implantation energy as a PLM processing parameter to the lifetime and concentration profile of the material, the concept of a bi-exponential decay rate with two lifetimes was introduced. Now, we will attempt to identify some relation between the two different lifetimes and two different regions of the concentration profile by exciting electrons at different depths in the material. If we excite closer to the surface pile-up, how will the lifetime value differ from that measured on the same sample at a deeper depth where the concentration of gold is less?

From our understanding of how our sample works when photoexcited, referring back to Ch.2.1, a higher concentration of dopant is going to increase the absorptance of our material. However, since these dopant atoms are foreign atoms with different electron energetics and atomic radius, they also are active recombination centers. The more dopants introduced, the electrons will recombine more quickly after photoexcitation. This is called trap-assisted recombination or Shockley-Read-Hall recombination, a theory describing that higher dopant concentration corresponds to faster
recombination, and thus a decrease in lifetime [16]. This relationship is observed in sulfur hyperdoped silicon shown in Figure 3.1.

![Figure 3.1: The change in excited carriers over time, comparing increasing concentrations of sulfur dopant. Figure adapted from Ref. [17].](image)

The fast recombination dynamics also depend on the depth at which our sample is excited or probed. This idea was experimentally tested in previous literature that probed a sample at two different depths by altering the absorption depth of incoming light with two different excitation wavelengths of 400 nm and 800 nm [14]. Figure 3.2 shows the results from Ref. [14], in which the fast lifetime when the sample is excited closer to the surface with 400-nm light (blue curve) is faster than when
excited at 800-nm light. This is clear if you look close at the comparison between the slope of the curves within the first 0.02 ns.

Figure 3.2: Decay in excited carriers over time between 400 nm vs 800 nm pump, showing both the simulation (solid line) and the experimental data. Figure adapted from Ref. [14].

For our samples, the different recombination mechanisms could be the result of a differing dopant distribution across depth. So far, it has been discussed the effects of implantation energy on the concentration profile. However, there are other factors as well. Those factors include surface oxide passivation, PLM fluence, and number of PLM processing shots. Passivating the surface of crystalline silicon is known to increase the efficiency by both decreasing surface recombination velocities and providing an anti-reflective coating [18]. The PLM fluence describes the energy of the melting laser, changing the melt depth, cooling velocity, and perhaps also causing
defects in the crystal structure. Lastly, the number of shots during PLM refers to how many times the melting and re-solidifying process occurs i.e. 1 time or 5 times. Some show that dopant profile distribution is deeper with more shots [19]. Both the PLM fluence and the number of shots have been shown to have effects on the concentration profile of a sample, as depicted in Figure 3.3. It is important to note that the samples in Figure 3.3 did not use ion implantation to introduce gold dopant; however, the comparison between the number of shots and fluences is still relevant. In summary, if we are attempting to show a connection between concentration and lifetime, we will want to consider these parameters later in experiment.

![Figure 3.3: Concentration profiles for the incorporation of Au in Si comparing the number of shots (A) and the PLM fluence (B). Figure adapted from Ref. [19].](image)

**3.2 Experiment**

Now, in order to test the connection between concentration and lifetime, we need to take lifetime measurements at different concentrations of gold dopant, in other words, we need to take lifetime measurements at different depths along the concentration
profile. The samples from Ch.2 were excited with 400-nm light, which corresponds to an absorption depth of roughly 100 nm into the samples. We want to probe closer to the surface, around a penetration depth of 5 nm. In this experiment, we choose to use an excitation pulse of 266-nm wavelength to achieve this. The absorption coefficient for 266-nm light in silicon is roughly $2 \times 10^6$ cm$^{-1}$; therefore, the absorption depth is $1/(2 \times 10^6$ cm$^{-1}$ ) = 5 nm roughly. Figure 3.4 shows the penetration depth of the two different pump wavelengths marked on the Au concentration profile of the sample implanted at 50 keV.

![Au Concentration Profile for 50 keV Implantation Energy](image)

Figure 3.4: Concentration profile for Au dopant in Si with penetration depths for wavelengths of 266 nm and 400 nm marked.
The experimental setup is identical to the 400-nm pump and THz probe detailed in Ch.2.2 except for the following part. After carefully aligning the light at 400 nm, three more optical crystals are inserted in the beam path to generate 266 nm. After the first nonlinear optical crystal converting 800-nm laser light to 400-nm light, a dual wave plate, a calcite compensator, and a second beta barium borate nonlinear optical crystal (BBO) are inserted in the beam path. These crystals rotate the polarization of the 400-nm light, and delay the arrival time with respect to the 800-nm fundamental beam before the BBO crystal generates sum harmonics (266 nm) from the incoming light (800 nm and 400 nm).

3.3 Results and Discussion

The experiment immediately showed faster lifetimes when the sample was excited with 266-nm light. Figure 3.5 plots the normalized decay data for both excitation wavelengths, where it is obvious that the 266-nm curve has a much steeper slope in the first 10 picoseconds. Thus, the fast lifetime corresponds to the surface pile-up of gold that is characteristic of the samples after PLM.
In order to strengthen this argument, the experiment was conducted with a set of six different gold hyperdoped silicon samples all with varying processing conditions (number of shots and fluences). The implantation energy and dose of gold dopant introduced was the same for all six samples (50 keV and $10^{15} \text{cm}^{-2}$). After fitting the data to Equation 2.6, the fast lifetime is roughly an order of magnitude faster at 266 nm compared to 400 nm. The fast lifetime is compared in Figure 3.6 for each sample.
3.4 Conclusion

The results of these six samples will not be compared individually to understand the effects of specific parameters. Rather, these results are used to verify a larger trend between fast lifetime and dopant concentration buildup close to the surface. Accounting for many processes that have effects on the concentration profile of our sample allowed us to confirm that it is truly the concentration profile that is affecting the surface recombination. The next step is to consider how very specific concentration profiles are affecting lifetime. This will be done through numerical simulation of lifetime dynamics in the next two chapters.
Chapter 4

Simulation Part 1

4.1 Introduction

The results in Ch.3 comparing the decay rate at 400-nm excitation pulse to that at 266 nm very decidedly confirmed that there is a faster decay rate when exciting closer to the surface. This finding inspired us to question the effects of the concentration profile on lifetime. There is obviously some correlation between a faster lifetime and a higher surface pile-up in the 266-nm vs. 400-nm experiment. However, this still does not give us a proper way of analyzing the lifetime value of a sample. What does a fast lifetime compared to a slow lifetime really tell us?

We can draw conclusions from experimental data, but if we could match simulated data to experiment, then we would have a deeper understanding of the physics underlying the observed behavior of a given parameter. This would also give us access to a valuable tool for predicting lifetimes of samples before experiment, allowing us to test what the best-fit parameters should be for the best sample. Ultimately, the possibilities with modeling are endless.
There are many researchers who use modeling techniques to simulate the behavior of hyperdoped silicon. For example, the equations that govern the PLM process are converted into numerical simulations to predict the concentration profile (Figure 1.6). Another example is the simulation described in Figure 3.2 where researchers simulated the comparison between lifetime of samples excited at different depths, using 800-nm and 400-nm light. Modeling is extremely useful for understanding how particular parameters, i.e. variables, affect the final outcome. Analytically solving an equation on pen and paper produces one result based on a defined set of variables. If such a solution is accessible, then we may use analytical techniques to vary different parameters. However, analytical solutions are not always possible. Instead, researchers use numerical simulations to best approximate the effects of varying a given variable while keeping the others fixed.

For these reasons, we chose to create a model to simulate the lifetime dynamics in hyperdoped silicon. The goal is to parse out which variables specifically alter the decay curve, focusing on the comparison between the fast decays. This will provide us with a better understanding of lifetime as well as a more efficient way of choosing those variables that must be bettered to increase the lifetime of a particular sample. These said variables will stem from equations for the diffusion and recombination of carriers over time in the sample, and will be outlined in this chapter as we walk-through the creation of our model.
4.2 Developing the Model

Figure 4.1 provides a nice visual goal of what we would like to accomplish with our model. The simulation in Figure 4.1 from Ref. [20] models excited carrier density in GaAs after photoexcitation. The terms that affect how many carriers are present after a certain excitation time is (1) bulk recombination life time $\tau_b$ and (2) surface recombination. Since recombination is enhanced by surface recombination when charge carriers are near the surface, diffusion of carriers away from this surface becomes an important parameter.

![Graph of the distribution of carriers across the depth of the sample, where each line represents a timestep of 50 ps. The inset graph depicts the normalized change in conductivity over time. Figure adapted from Ref. [20].](image_url)
Equation 4.1 shows the exact equation that Figure 4.1 models. The first term on the right hand side of the equation is electron diffusion, the second is bulk recombination and the third term is the initial condition. The third term is only nonzero at time zero, and is represented by an exponential to describe the decay distribution of how light is absorbed in the material.

\[
\frac{\partial n}{\partial t} = D \frac{\partial^2 n}{\partial x^2} - \frac{n}{\tau_b} + \delta(t)e^{-\alpha x}
\]  

Where D is the diffusivity of gold in silicon, \( \tau_b \) is the bulk recombination lifetime, \( \alpha \) is the absorption coefficient, and \( \delta \) is a delta function describing the power absorption of the radiation from the excitation pulse.

The inset graph of Figure 4.1 shows the model solution for the change in conductivity over time plotted against the experimental data, confirming that the fit is good. The inset graph depicts a decay that is not single-exponential, which is the unique dynamic we want to build into our own numerical modeling. Thus, we will take this equation as the base for our model. However, we will modify it slightly. Firstly, the third term will be removed because we will set up an initial condition for the density of carriers across depth at time zero. Secondly, since we are determining effects of concentration profiles on lifetime, the bulk recombination lifetime term will be spatially dependent. Furthermore, unlike Ref. [20], surface recombination is
neglected in our model. Thus, modifying Equation 4.1 to fit our needs, we get
Equation 4.2 for our numerical simulation of the density of carriers \( n_e \) over time.

\[
\frac{\partial n_e(x, t)}{\partial t} = D \frac{\partial^2 n_e(x, t)}{\partial x^2} - \frac{n_e(x, t)}{\tau_b(x)} \tag{4.2}
\]

4.3 Numerical Process in MATLAB

The model was coded in a MATLAB live script, an easily accessible language that may be cleaned up for future use as a theoretical tool in the lab. The live script platform in MATLAB allows for section breaks, titles, and in-text descriptions for each step in the modeling process. Consecutive steps of the code are described to fully outline the modeling process.

4.3.1 Initial Condition

The first step is to calculate the initial profile for the electron density across the depth of the sample at time zero after excitation. Notice that Equation 4.3 for the initial profile is in the same format as the third term in Equation 4.1.

\[
n_e(x) = n_0 e^{-ax} \tag{4.3}
\]
Where $\alpha$ will be initially defined as the absorption coefficient for 400-nm light in silicon, and $n_o$ is a proportionality constant that we must calculate so that the area under the curve of our initial profile is equal to the number of photons per area.

\[
\int n_e(x)dx = \frac{n_{\text{photons}}}{A}
\]  

(4.4)

Where $A$ is the area of our sample that is illuminated by the excitation pulse. And the number of incoming photons may be calculated from the incoming laser excitation energy.

\[
n_{\text{photons}} = \frac{\text{Energy per pulse}}{\text{Energy per photon}} = \frac{\text{Pump power} \ast \lambda}{\text{Pulse Rate} \ast h \ast c}
\]  

(4.5)

The initial profile is plotted in Figure 4.2, showing the distribution of electrons across the depth of the material at time zero. How this profile will change after time zero will depend on how the carriers diffuse and recombine across the depth of the sample.
4.3.2 Diffusion

The model was built with only diffusion at first to verify that it was working properly before adding in recombination later. Thus, we first focus on the diffusion term.

\[ D = \frac{\mu k_B T}{|e|} \]  

(4.6)

The diffusivity (D) is defined in Equation 4.6 from the mobility of electrons in silicon and constants where T is room temperature (300 K) [20]. These constants are simply
defined within the script as one constant multiplied by the mobility, because we will vary only mobility to see effects of changing diffusivity on lifetime.¹

4.3.3 The Forward Time Center Space (FTCS) Numerical Method

The next step is to model the temporal and spatial evolution of the electron density, where the electron density will be calculated over distance in increments of dx and time in increments of dt. The discrete points in the model for \( n_e(x,t) \) will be replaced by an index of \( k \) for time and \( j \) for space. We will use a method called the Forward Time Center Space (FTCS) finite difference scheme that is derived from the Taylors series expansions. This method converts differential equations into a form that may be numerically solved. Higher order terms are dropped and the derivatives in time \((d/dt)\) and space \((d/dx)\) are approximated as first and second order difference operators. With some manipulation, we get the FTCS solution:

\[
N_j^{k+1} = N_j^k + s(N_{j-1}^k - 2N_j^k + N_{j+1}^k) \tag{4.7}
\]

Where \( s \) is the diffusion term that we define as

\[
s = D \frac{\Delta t}{\Delta x^2} \tag{4.8}
\]

¹ A table with all constants used to create the model will be provided in Ch.4.4
and the indicial notation comes from the Taylors series approximations at different steps:

**Spatial**

<table>
<thead>
<tr>
<th>Replace</th>
<th>(n_e(x - \Delta x))</th>
<th>(n_e(x))</th>
<th>(n_e(x + \Delta x))</th>
</tr>
</thead>
<tbody>
<tr>
<td>With</td>
<td>(N_{j-1})</td>
<td>(N_j)</td>
<td>(N_{j+1})</td>
</tr>
</tbody>
</table>

**Temporal**

<table>
<thead>
<tr>
<th>Replace</th>
<th>(n_e(t - \Delta t))</th>
<th>(n_e(t))</th>
<th>(n_e(t + \Delta t))</th>
</tr>
</thead>
<tbody>
<tr>
<td>With</td>
<td>(N^{k-1})</td>
<td>(N^k)</td>
<td>(N^{k+1})</td>
</tr>
</tbody>
</table>

In MATLAB, this solution is set up with what is called a ‘for loop’. It is essentially a loop over a set of equations. The number of loops is defined by a start, end, and step size. In this case, we are calculating over time in picoseconds. The loop then will calculate the set of equations at each time step from zero to the set simulation end. We start by defining an empty matrix in which the columns represent depth from 0 nm to 300 nm and the rows represent each point in time.

Using the final FTCS solution, we loop over this equation to slowly fill in the empty matrix. By changing the timestep, we can get excitation density across depth at every picosecond, every 10 picoseconds, etc. for however long we care to run the simulation. So far we have only modeled the diffusion of carriers. After confirming the model was working, more complexities may be added.
4.3.4 Recombination

We must account for bulk recombination, the second term in Equation 4.2. From Equation 4.2, we have that the recombination term is the electron density over the lifetime. We will break this down further into the required variables used in the modeling process.

\[ \frac{1}{\tau_B(x)} = v_{thermal} \cdot A_{xsec} \cdot n_{Au}(x) \]  

(4.9)

Where \( n_{Au} \) is the density of dopant atoms at a given depth and the velocity is a constant defined as

\[ v_{thermal} = \sqrt{\frac{3k_B T}{m}} \]  

(4.10)

And the capture cross section may be manipulated similarly to the mobility for fitting and the dopant concentration across the depth will vary based on the particular sample. The Au concentration profile of the sample that is being modeled is loaded in before the for loop and then interpolated so that at each depth, the code calls in the correct matching concentration measure at that depth (Figure 2.2 and Figure 3.4).
4.3.5 Decay in Number of Excited Carriers over Time

Lastly, the goal is to have a graph that may be compared to the experimental plots of normalized decay rate over time in picoseconds, as is done in the inset graph of Figure 4.1. Thus, we graph the density of electrons across the depth of the material at each point in time. The total number of carriers is the area under the plot of electron density across depth. Thus, taking the sum of each row vector as one point corresponding to a time and normalizing the data to 1 gives us the final Figure 4.3.

![Normalized Simulation](image)

**Figure 4.3:** Normalized Simulation of decay in excited electrons over time where the timestep is 10 ps.
The simulation successfully produced a non mono-exponential trend. And the connection to the concentration profile can immediately be proved by running the simulation with (1) a nonuniform concentration profile with a surface pileup and (2) a uniform concentration profile. These two simulated decays are plotted together for comparison in Figure 4.4. The y-axis for the normalized change in excited carriers is log-scaled to highlight the fact that the uniform Au profile decay may be fit to a single-exponential.

Figure 4.4: The log plot of the simulated decay for the 50 keV sample comparing effects of a uniform vs. nonuniform distribution of gold dopant across depth.
4.4 Simulation Constants

<table>
<thead>
<tr>
<th>Model Variable</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pump Power</td>
<td>0.002</td>
<td>W</td>
</tr>
<tr>
<td>Pulse Rate</td>
<td>1000</td>
<td>Hz</td>
</tr>
<tr>
<td>h</td>
<td>6.626E-34</td>
<td>Js</td>
</tr>
<tr>
<td>c</td>
<td>3E17</td>
<td>nm/s</td>
</tr>
<tr>
<td>A</td>
<td>0.0154E14</td>
<td>nm²</td>
</tr>
<tr>
<td>k_B</td>
<td>1.380E-23</td>
<td>J/K</td>
</tr>
<tr>
<td>T</td>
<td>300</td>
<td>K</td>
</tr>
<tr>
<td>m</td>
<td>9.108E-31</td>
<td>kg</td>
</tr>
<tr>
<td>e</td>
<td>1.602E-19</td>
<td>C</td>
</tr>
</tbody>
</table>

Table 4.1: A table of constants for the variables used in the creation of the model. Pump power, pulse rate, and spot size (A) are all measured in the lab. The rest are literature values adapted from Ref. [21].

4.5 Conclusion

Finally, we now have a model with diffusion and bulk recombination that provides a simulated plot that may be compared to experiment. In Ch.5, the simulated lifetime plots will be compared to each other and experimental data to provide an idea on how changing the wavelength of the excitation pulse, the mobility of the carriers during diffusion, and the capture cross section all can affect how fast lifetime is. Most importantly, it will become clear the significance of the concentration profile on lifetime dynamics.
Chapter 5

Simulation Part 2

5.1 Introduction

The modeling process in Ch.4 highlighted variables that were to be manipulated in the fitting process as well as proving that a nonuniform concentration profile is what creates the non-mono-exponential decay. The first step in using this model to simulate our specific samples is fitting to data. The carrier dynamics and dopant distribution of one sample set is first used in this model in order to fit the carrier mobility and capture cross section. In this case, Si:Au sample at 50 keV implantation energy is used because data at both 400-nm and 266-nm pump wavelengths are available for comparison (Ch.3). Through trial and error, the model was run multiple times while varying either the capture cross section or the mobility to manipulate the diffusion and recombination terms until a best fit possible was reached with experimental data. After the best parameters were identified for a good fit, carrier dynamics data for the Si:Au samples implanted at 100 and 300 keV (Ch.2) was fit to the same carrier mobility and capture cross section. This chapter will walk through the outcome of our model and the analysis of how it fits alongside experiment as well as the future directions that may be taken with this simulation.
5.2 Fitting Parameters

First, we began with a reasonable fixed capture cross section of 0.01 nm$^2$ for gold in silicon, which is a literature value obtained at very low gold doping concentration [22]. Then, the model was run while varying mobility only. The two graphs in Figure 5.1 depict the difference in diffusion of carriers when we increase the mobility by a factor of 10. Notice that for a mobility of 100 cm$^2$V$^{-1}$s$^{-1}$ (units for velocity over electric field), all the carriers have diffused across the depth within 3 picoseconds. However, the electrons diffuse much more slowly at a low mobility of 10 cm$^2$/V/s; the profile of electron density has not changed greatly within 3 ps compared to the more spread out profiles at mobility 100. The comparison between low mobility (10) and high mobility (100) in Figure 5.1 depicts the effect of changing mobility on the diffusion of electrons in the material.
Figure 5.1: Comparison of diffusion across depth between increasing mobility
Now when comparing against the experimental data, remember that the simulated decay is the area under the curve at different time steps normalized to the area under the curve initially \(t = 0\) (Figure 4.2). Figure 5.2 shows simulated carrier dynamics. At each point in time, the area under the curve shown in Figure 5.1 corresponds to the number of electrons probed by THz, and Figure 5.2 shows how this number changes over time. We test three different mobilities of 10, 30 and 100 to find the best fit possible. It is clear from Figure 5.2 that changing mobility affects the lifetime only after about 10 picoseconds, which we call the tail. Varying mobility, and thus varying the diffusivity of carriers, does not greatly change the fast lifetime dynamics.

![Mobility Comparison (Capt.Cross 0.01)](image)

Figure 5.2: Simulated lifetime with different carrier mobility. The raw data is the 266-nm experimental curve shown in Figure 3.5.
Next, we move to the recombination term with a fixed mobility of 100, chosen mostly because it lines up well with the tail of experimental data. The idea is that the recombination term will have larger effects on the fast lifetime. The model was tested with four different capture cross sections ranging from the original of 0.01 to 0.1 nm$^2$, a magnitude greater. Figure 5.3 plots the comparison of the four simulated decays to experimental data. The prediction that varying the recombination term would have greater effects on the fast lifetime is correct. The larger the capture cross section, the faster the recombination is and thus the faster lifetime decay. This is consistent with theory. The capture cross section denotes the area of influence these recombination sites have on the electrons moving past them. As the capture cross section is increased, the likelihood of recombination will increase, which in turn gives rise to a faster lifetime.
The next question was how to optimize these two different parameters to fit well with both this initial fast lifetime and longer tail. This was a difficult task and after much trial and error, we noticed that we can only fit those first 10 picoseconds or so well. It was nearly impossible to find a good fit for the tail. Without having to simulate out to roughly 1500 ps, which is the experimental time window, we already recognize that there is definitely a factor contributing to the decay that is not accounted for in our model (Figure 5.4). Although the model is not perfect, it is a very good approximation and a step towards a better understanding of the factors affecting lifetime.
We decided to optimize the simulation to best fit the short portion of the lifetime. The choice to focus on the fast lifetime fit was made in order to show future analyses that relate to the surface recombination rate that is being affected by the surface pile-up in the concentration profiles. This fit is done with the 266-nm pump-probe data for the 50 keV Au implanted silicon with high fluence and 1 PLM shot. As a result, the best fit parameters are with mobility of 120 cm$^2$/V/s and capture cross section of 0.02 nm$^2$.

Without changing any of the fit parameters, we simulate the decay when the excitation wavelength is 400 nm. At this wavelength, the pump light penetrates the sample much deeper (Figure 3.4), so diffusion and initial recombination near the surface are all different. It may be proven that the model works very well. The only difference between the two simulated curves is the wavelength of the excitation pulse corresponding to different light absorption coefficients (Ch.4.3.1). From the comparison between the two simulated decays plotted on top of the corresponding experimental data, it is clear that these same best-fit values work for different samples. The wavelength dependent carrier decay dynamics validated the model we built.
5.3 Simulating Lifetime at Increasing Ion Implantation Energy

After verifying the fit of these chosen values, the model was run for the three samples at different implantation energy and similarly plotted against the experimental data. All the samples were implanted by the same dose of gold, but the gold ions were accelerated to different energies (50, 110, 300 keV), and hence the dopant distribution profiles are different between these samples. The Au distribution is much deeper (~150 nm) when the implantation energy is much higher. It must be noted that these best fit parameters were fitted to the sample with an implantation energy of 50 keV with optical excitation at 266 nm and not refit for each sample.
Figure 5.5 shows the comparison between the simulated and experimental decay. In the experimental data, there is only a small difference between the 50 keV implant and the 110 keV implant, and our simulation shows the same trend. The simulated curve for the 300 keV sample, however, decays much slower than the actual experimental result. In order to fit the simulation to the data, the capture cross section had to be increased in the recombination term by a factor of 10 to speed up the decay in the first 10 picoseconds. Both the original fit and the fit with the new capture cross section for the 300 keV are plotted in Figure 5.5.

![Figure 5.5: The normalized decay from the simulation and experiment comparing implantation energy.](image)

A possible reason why the 300 keV sample exhibits a much faster lifetime, which cannot be simulated by changing the Au concentration profile, relates back to the
discussion in Ch.2.4. A higher implantation energy is slamming gold ions into the silicon at an intensity six times that of 50 keV. Such a force is more likely to cause defects and damage in the sample that cannot be removed by the PLM process after ion implantation. Thus, the faster lifetime for the 300 keV sample may come from lattice defect in addition to the Au dopant in the sample.

Increasing the capture cross section by a factor of 10 largely increases the recombination term. As a result, the electron distribution is very sensitive to the Au dopant distribution profile, which can be seen in Figure 5.6. In Figure 5.6, there are two bumps, a local maximum near 50 nm and a local minimum near 150 nm. These two bumps are mirrored in the Au dopant concentration profiles: Figure 2.2 shows that aside from the initial surface pile-up, locally the Au concentration is highest at 120 nm. In this case where recombination is severe, the electron distribution in Figure 5.6 will exhibit a dip at the same depth.
Although this is an interesting point to make regarding the difference at 300 keV, the main takeaway is that the simulation of samples with different implantation energies under the same parameters follows the expected trend in the data. For the rest of analysis, we will return to using the same fit parameters for all three samples.

The next question to be asked of the simulation is whether there is any sense to be made of the experimental data from Ch.2 on lifetime that conflicted with the results of Ch.3. In Ch.3 when comparing 266 nm and 400 nm pump-probe data, our result provided evidence for a surface effect on recombination, which we credited to the surface pile-up seen in the concentration profile. However, the SIMS data (Figure...
that was taken for the three implantation energies showed the opposite: those profiles with a higher pile-up (50 keV sample) at the surface actually had a ‘better’ i.e. longer lifetime (Figure 2.5 and 5.5). Although we did not carry out a 266 nm vs. 400 nm experiment for samples at 110 keV and 300 keV implantation energy, we may attempt to simulate them.

Figure 5.7 shows the simulated decays for the three samples of different implantation energies with a 266-nm pump. Although the 300 keV sample had different best fit parameters, all three samples were fitted with same parameters so as to make a consistent qualitative comparison between 266 nm and 400 nm. The only other factor that is changing between the samples is the concentration profile.

Figure 5.7 shows the trend we would expect in fast lifetime when probing the surface region of the concentration profile. In the first 10 picoseconds, the pattern has now flipped compared to the 400 nm data plotted in Figure 5.5. The sample implanted with an energy of 300 keV, that has the smallest surface pile-up out of the three samples, now has the slowest fast lifetime. With this model, we have now confirmed that the direct proportionality between increase in concentration and decrease in lifetime holds true for the samples at different implantation energies as well.
5.4 Conclusion

The initial goal of this modeling process was to prove that the concentration profile is the cause of the bi-exponential decay that we see, and that it may possibly be from a combination of diffusion and this one lifetime that is concentration-dependent. The figures in this chapter have provided convincing evidence for this statement. The largest takeaways from this process is one, our model works in that it qualitatively follows the trends we see in experiment, and two, the decrease in lifetime when probing at depths where there are higher concentrations of gold dopant in the profile validate our hypothesis. This model in its elementary and simple stage provides the
groundwork for a powerful theoretical tool in identifying optimal concentration profiles for increasing the lifetime of hyperdoped silicon.
Chapter 6

Conclusion

6.1 Summary

The goal of this thesis was to identify the interplay between the dopant concentration profiles created by different PLM process parameters and the charge carrier lifetime of the material through both experiment and modeling. Initial lifetime fitting for experimental data introduced the idea of bi-exponential decay and was believed to be the effect of fast recombination dynamics occurring at the surface of the sample, corresponding to the characteristic pile up of gold dopant. The 266-nm vs. 400-nm experiment was created to test this theory and subsequently confirmed that faster lifetime occurred when probing closer to the surface pile up of gold dopant.

The second half of this thesis tackled a numerical approach of modeling the lifetime dynamics with bulk recombination and diffusion. The recombination term was depth-dependent on the gold concentration profile. The numerical simulation results were not perfect, but successfully showed that (1) the bi-exponential decay behavior stems from a non-uniform Au concentration profile and (2) reproduced experimental trend on the short time scale. Comparing simulation and experiment allows us to identify that at large ion-implantation energy, additional recombination channels not directly
related to Au concentration need to be taken into account. A likely candidate for such a recombination channel could be lattice defect. The complexities of lifetime dynamics may not be explained by these results, but both experiment and numerical simulation have confirmed that the nonuniform concentration profile created by pulsed laser melting causes this very fast decay in electrons within the first 10 picoseconds after excitation.

6.2 Future Directions

The introduction of Ch.5 outlined the significance of models in the theoretical work behind many different branches of research. The lifetime dynamics simulation created for this thesis will be used in future analyses as well as predictive work for discovering what is the ideal concentration profile to maximize lifetime in gold hyperdoped silicon. As it goes for any model, there is an unlimited list of complexities and variables and functions that may be added to increase the precision of the model. However, for starters, it may be deduced that PLM may not be the best method for creating hyperdoped samples. Let us look to flash lamp annealing or surface etching to remove dopant pile-up. The future of gold hyperdoped silicon seems promising if we combine both experimental work and numerical modeling to efficiently move towards a better method for the incorporation of gold in silicon.
Bibliography


