Photoconductivity and Minority Carrier Lifetime
in Tin Sulfide and Gallium Arsenide Semiconductors for Photovoltaics

by

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Abstract

The growth and maintenance of the modern technological world requires immediate solutions in the field of clean, renewable energy. One prominent solution is the rapid advancement of solar cell technologies due to the wide availability of solar energy and the growing versatility of harnessing it. As efficiencies for these devices creep upwards, it becomes increasingly more important to find the greatest inhibiting factor. Through a solar cell simulator program (SCAPS), improvements in the minority-carrier lifetime of cell materials show not only significant improvements in cell efficiencies, but also an un-masking of improvements by other properties, which are inhibited when the lifetime is too short. This work aims to calculate the mobility-lifetime products ($\mu\tau$) of gallium arsenide (GaAs) and annealed and un-annealed tin sulfide (SnS) with respective $p$-doping carrier concentrations of $10^{18}$ cm$^{-3}$, $10^{16}$ cm$^{-3}$, and $10^{15}$ cm$^{-3}$ through photoconductivity measurements. Films are 1 $\mu$m thick and have a four-bar and two-bar contact configuration to model carrier conductivity as a sheet. For calculations, two methods of modeling charge carrier generation are considered; a uniform generation throughout the film and a depth and wavelength-dependent generation. This work found values on the order of $10^{-1}$ cm$^2$ V$^{-1}$, $10^{-4}$ cm$^2$ V$^{-1}$, and $10^{-5}$ cm$^2$ V$^{-1}$, for GaAs, annealed SnS, and un-annealed SnS, respectively, for both methods of calculation. The simplified approach considering a uniform generation yielded lower results than the depth and wavelength dependent calculations by about a factor of two. All values were three to four orders of magnitude higher than those found in the literature. For this reason, it is believed that the majority-carrier is dominating measurements due to an inhibited minority-carrier lifetime.

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1. Introduction

1.1 Motivation

The modern rate of energy and material consumption and waste is unsustainable. Developed nations currently enjoy a lifestyle only possible through the advancements made during the industrial age. However, developing nations are fighting to reach this same standard of living while burdened by the environmental costs of the Western world’s advancement but unable to make similar sacrifices. Current methods of energy production are moving towards cleaner and safer sources, but not at rates fast enough to sustain growing global energy demands.

Solar is one of the most promising and fastest growing renewable energy sources in the field due to its versatile potential. While renewable energy sources such as wind or geothermal are strongly limited by geographical location, solar energy can be utilized nearly anywhere on the earth’s surface with around 36,000 TW of available solar resource [2]. Given that the global energy consumption is around 16 TW [2], the benefit of advancing solar energy harvesting technologies and pushing up cell efficiencies becomes obvious. With further technological advancements, solar energy can also be integrated into common items of everyday life.

According to the Shockley-Queisser Limit, no single p-n junction solar cell, discussed in Chapter 2.4, will be able to obtain 100% conversion efficiency - the highest theoretical efficiency is around 33% for a band gap of 1.3 eV, shown by the lowest curve in Figure 1-1. Current single-crystalline solar cell modules have achieved efficiencies around 25% [14]. Other methods have sought to surpass this efficiency by utilizing different band gaps and material absorption properties in layers, called tandem cells. Unfortunately, the production expenses of such cells often outweigh the benefits of their increased efficiency.
The methods pursued in this thesis explore one of the most important and less documented factors affecting device efficiency – minority-carrier lifetime ($\tau$). This is a measure of how long the minority charge carrier, an electron or hole, exists within a material. This will be analyzed in conjunction with the carrier mobility ($\mu$), the speed with which the carrier moves, through measurements of the material’s photoconductivity ($\sigma$), explained further in Chapter 3.

The minority-carrier lifetime is a very important property for solar cells because it determines the likelihood that a charge carrier will be collected by a metal contact, or electrode on the cell, and therefore used for energy conversion. A longer lifetime in a solar cell typically means a greater likelihood of collection. For this reason, a longer lifetime also correlates to a larger efficiency. Preliminary work for this thesis to observe the importance of lifetime on cell efficiency was done on a solar cell simulator called SCAPS. Some of this work can be seen in Chapter 2.2 and a brief explanation of the SCAPS program is given in Chapter 4.5.

![Figure 1-1: Solar Irradiance Spectra 1.5 for 1.1 eV bandgap. The majority of available light is unusable for solar energy conversion. The beige area corresponds to the Theoretical Shockley-Queisser Limit. [19]](image-url)
Charge carrier lifetime can be difficult to measure, particularly since the time scale is on the order of a couple of nanoseconds. This thesis will explore one technique to experimentally determine the photoconductivity of \( p \)-doped tin monosulfide (SnS) and gallium arsenide (GaAs) and computationally acquire the product of charge carrier mobility and lifetime (\( \mu \tau \)) of these materials. The computational approach to determining the mobility-lifetime product will use both a simplified computation as well as a more complex one, intended to build-upon current procedures for photoconductivity measurements. It is hoped that this work will contribute to solutions for efficiency limitations of SnS absorber layers in solar cells.

GaAs has been a popular material for solar research due to its theoretical efficiency limit around 30% and high carrier mobility \([10]\). It was chosen as a reference material to assure the reliability of the machine and techniques.

SnS is not as well researched or processed as GaAs. It has both a direct and indirect band-gap, which offers the potential for strong optical absorption, characteristic of direct band-gaps, and longer minority-carrier lifetimes, due to the phonon barrier of indirect band-gaps. The physics of this will be discussed further in the next section. Finally, SnS is a nontoxic, abundant material, which does not require very high temperatures for film fabrication.

2. Background Physics

2.1 Energy Bands

First, it is necessary to discuss the conductive mechanisms of semiconductor materials. According to Bohr’s model of an atom, electrons exist fixed within an orbit of a specific geometry and energy around a nucleus. These orbits are called electron clouds and movement of an electron between clouds is only allowable with quantized changes in energy.
While Bohr’s atomic model describes electron movement and placement around an atom, it does not consider how atoms interact when closely packed in a solid. The small atomic spacing of a crystallographic arrangement causes the electron clouds of atoms to overlap. In metals, this electron level overlap occurs across so many energy levels, that electrons are able to move freely throughout the solid. Because of this, metals are strong conductors.

![Figure 2-1:](image)

In semiconductor materials, the electron cloud overlap is not so comprehensive, though there is still considerable interaction. The electron levels of the atoms within the clouds merge to form two specific bands, called the valence and conduction bands. A schematic of this for metals, semiconductors, and insulators is shown in Figure 2-1. First, the valence band is the lower energy grouping, where electrons are immobile. If enough energy is supplied to a bound electron in the valence band, it can be “excited” into the conduction band, where it is able to move freely throughout the material. A possible source of energy for excitation is a photon, or
particle of light. Mobile electrons in the conduction band leave holes in the valence band. Both charge carriers in their respective bands contribute to a material’s conductivity.

![Diagram of energy bands]

**Figure 2-2: Representation of Valance and Conduction bands.** An indirect band-gap (right) will need a phonon contribution in addition to a photon in order for carriers to traverse the band-gap. This can inhibit absorption. [7]

The energy spacing between these bands is known as the band gap. In a pure semiconductor material, no energy states can exist within the band-gap and all electrons in the conduction band will have energy equal to or greater than this gap energy. The conduction and valence bands simply identify the boundaries of these available energy states but they are not themselves discrete energy levels. An insulator has a similar band structure to a semiconductor, except the band-gap is so large that very few electrons are able to be excited across it at room temperature.
Figure 2-2 shows two possible band structures in a semiconductor; a direct band-gap and an indirect band-gap. The direct band-gap requires only the energy of this band edge difference to excite an electron across it. However, an indirect band-gap requires both this energy and a phonon contribution to overcome the change in momentum required for band transition. A phonon is a quantum of energy associated with the vibration of a crystal lattice. Excitation or relaxation across an indirect band-gap is less likely to occur than across a direct band-gap due to this phonon requirement. As such, direct band-gaps are known for high absorption and indirect band-gaps are known for longer lifetimes.

As an example, let’s look at the most well-known semiconductor material, silicon (Si), which has a direct band-gap energy of 1.1 eV, or $1.76 \times 10^{-19}$ J. The quantized energy of a single photon of light is $\frac{h \cdot c}{\lambda}$, where $h$ is Plank’s constant, $c$ is the speed of light, and $\lambda$ is the wavelength of the photon. Just within the visible range of the Sun’s spectrum, $\lambda$ is between 400 and 700 nm, so the associated energy is between $2.8 \times 10^{-19}$ J and $4.9 \times 10^{-19}$ J. This is more than enough energy to generate carriers in Si!

### 2.2 Doping

In the real case, there are many levels within the band-gap that can influence the concentration of electrons and holes in the conduction band and the valence band. One way to intentionally do so is to dope the material. Doping creates donor or acceptor levels, which are able to contribute an electron or a hole, respectively, to their corresponding conduction bands, as shown in Figure 2-3.

To dope a material is to introduce atoms of another element with a higher or lower charge than what exists in the crystal lattice. A common doping pair is Si and boron (B), or Si and
phosphorous (P). On the periodic table, Si is a group IV element, B is group III, and P is group V. For this reason, B has one additional positive charge associated with it than Si and P has one additional negative charge. Therefore, doping Si with B causes the material to be positively doped, or \textit{p}-doped, while doping Si with P causes it to be negatively, or \textit{n}-, doped.

![Diagram of \textit{n}-type (a) and \textit{p}-type (b) doped semiconductors.](image)

\textbf{Figure 2-3}: Diagram of \textit{n}-type (a) and \textit{p}-type (b) doped semiconductors. The donor energy level within the band-gap of (a) donates electrons to the conduction band. Similarly, the acceptor level of (b) accepts electrons and leaves conducting holes in the valence band. [6]

In the case of SnS, doping tends to come from vacancies, or missing atoms, in the material. An S vacancy is associated with a negative charge and a Sn vacancy with a positive. For this reason, when vacancies of one type are reduced, it causes a relative increase in the other type, effectively doping the material. For one of the SnS samples of this work, annealing in a S rich environment caused a decrease in S vacancies, which doped the material as \textit{p}-type [5].

While electrons and holes typically come in pairs, doping allows one to be in excess. The carrier in excess is called the majority charge carrier, counter to minority charge carrier.

\textbf{2.3 Recombination and Traps}

For a free carrier in the material, there are three possible things that can occur; it can be collected by an electrode, it can recombine with its charge pair, or it can become trapped. When
an electron-hole pair recombines, it “no longer exists” because it is no longer contributing to the conductivity of the material. Recombination occurs when a free carrier electron meets a free carrier hole and fills it. This electron then drops down to a lower energy level on an atom, returning to the valence band of the material.

Trapping is similar to recombination in that it prevents the movement of charge carriers, but unlike recombination, it is not a permanent occurrence. With some thermal energy, the carrier is re-emitted back into the original band after some time. The probability of re-emission is often equal to the probability of capture [1].

Trapping and recombination occur at sites within the material dubbed “trapping sites” and “recombination sites” depending on the type of interaction that will likely take place there. If a trap is particularly strong, such that the probability of the trapped carrier recombining with a carrier of opposite sign is greater than the probability of the trapped carrier being thermally freed from the trap, it will be a recombination site and vice versa for the opposite case. Often times, a recombination site under one illumination and temperature may be a trapping site at another due to the change in thermal energy contribution on the sample [1].

Radiative recombination can occur anywhere in the material when an electron meets a hole and falls back down to the valence band. However, trapping and recombination sites are present due to defects in the material. A defect is the presence of an imperfection in an otherwise perfect crystal lattice. This can be the S vacancies present in the SnS material, “dangling” bonds at the surface of the material, or dangling bonds or lattice mismatch at the interface between two grains in a crystal, called a grain boundary. Materials with fewer defects will have a lower probability of recombination for its charge carriers and incidentally, a longer charge carrier lifetime. If the likelihood of dying is lower, the carrier will live longer.
Another thing to consider when observing defects and trapping/recombination sites, is the capture cross section ($S_{\text{capture}}$) of the site. The capture cross section relates to the variation of potential around the site, which causes trapping to occur. If the binding energy of coulomb attraction is greater than the thermal energy of the carrier, the carrier will become trapped [1]. In this way, if the site, or center, is charged, it will preferentially capture the carrier with the opposite charge. The relationship between $S_{\text{capture}}$ and $\tau$, can be shown by:

$$\tau = \frac{1}{vN S_{\text{capture}}}$$

(1)

where $v$ is the mobility of the charge carrier, and $N$ is the number of recombination centers per unit volume which can capture a charge carrier. As $S_{\text{capture}}$ increases, or as the preference of capturing one charge over another increases, the $\tau$ of that preferred charge carrier will decrease.

In a semiconductor, measuring the minority-carrier lifetime is possible due to the relative changes of photo-excited charge carriers compared to intrinsic charge carriers. If the density of charge carriers in a material is much larger than the density of recombination centers, then the limiting factor to conductivity will be the minority-carrier. Conversely, if the density of recombination centers is larger, nearly all minority charges will be recombined and the majority-carrier will dominate the photoconductivity signal, as is often the case for insulators.

### 2.4 Basics of a Solar Cell

A solar cell can be formed when a $p$-type and an $n$-type semiconductor are placed together, creating a $p$-$n$ junction. The difference in charge carrier type causes a flow of carriers across the interface between the two materials until enough recombination has occurred, that a neutral barrier forms, called the depletion zone, or space-charge region. An electric field exists across this zone, which prevents most additional recombination events.
Figure 2-4 shows a $p$-$n$ junction in the dark under no applied voltage. The net flow of carriers across the junction, or the current, is equal to zero. The total current is the result of carriers moving in both directions across the space charge region. Diffusion current occurs when a charge diffuses across the potential barrier, to the side of majority opposite charge – an electron diffusing from the $n$ to the $p$ side. Drift current occurs when a minority-carrier is generated near the space charge region, travels into it, and is propelled by the electric field towards the side with positive like charge – an electron generated on the $p$ side reaches the edge of the space charge region and is sent to the $n$ side of the device.

![Figure 2-4: Screenshot of a $p$-$n$ junction simulation in the dark. Carriers move across the depletion, or space charge, region through diffusion and drift. Net current is zero under zero voltage. [18]](image)

Applying a voltage across this junction can either raise or lower the depletion zone barrier for charge flow. A forward bias voltage will decrease the electric field across the barrier.
and thus raise the diffusion current, while a reverse bias will do the opposite. The diffusion current is driven by recombination events.

The diode equation is given by:

\[
I = I_0 \left( e^{\frac{qV}{kT}} - 1 \right)
\]

where \( I \) is the net current, \( I_0 \) is leakage current in the dark, strongly dependent on recombination, \( q \) is the charge of an electron, \( V \) is applied voltage to the junction, \( k \) is the Boltzmann constant, and \( T \) is the temperature of the device. The diode equation models the current of the device in response to an applied voltage. In the light, the equation becomes:

\[
I = \left( I_0 \left( e^{\frac{qV}{kT}} - 1 \right) \right) - I_L
\]

where \( I_L \) is the photo-generated current. The resulting current verses voltage (IV) curve for both equations can be seen in Figure 2-5.

![Figure 2-5: Current-Voltage (IV) curve for a p-n junction under dark (blue) and illuminated (orange) conditions. \( T = 300 \text{ K}, I_0 = 10^{-8} \text{ mA}, \text{ and } I_L = 2 \text{ mA.} \)](image)
The most important aspects of an IV curve under illumination are the x- and y- axis intercepts and the point on the curve, which fills the maximum possible rectangle beneath the curve. The y-axis intercept is called the shore circuit current ($I_{SC}$) and corresponds to the maximum possible current the solar cell achieves under zero voltage bias. The x-axis intercept is the open circuit voltage ($V_{OC}$) and corresponds to the maximum possible voltage achieved with zero current. Both are indicated in Figure 2-6. $V_{MP}$ and $I_{MP}$ identify the voltage and current at which maximum power is achieved. Their product creates the maximum possible rectangle area beneath the IV curve.

![IV curve diagram](image)

**Figure 2-6:** Close-up of the illuminated (IV) curve from Figure 2-5.

Taking the area of this rectangle identifies the maximum power achievable by the cell. The Fill Factor (FF) is a ratio of this maximum power and the product of $V_{OC}$ and $J_{SC}$. Maximizing the FF is desirable since this corresponds to a large generated power for the device.

All basic solar cell concepts, as well as many of the more complex ones, can be found at
Chapter 3. Charge Carrier Lifetime and Photoconductivity

3.1 Introduction to Lifetime

The minority-carrier lifetime is simply how long an excited electron or hole exists or survives in the material before being recombined, collected, or trapped. There are benefits to having a long or short lifetime, depending on the desired device characteristics. For solar cells, a long lifetime is better because it will increase the likelihood of the carrier being collected by a metal contact. A longer lifetime can be achieved with a very pure material with minimal defects or recombination sites.

3.2 Influence of Lifetime

The following graphs exhibit a few examples of the effect of carrier lifetime on device efficiency. The change in one parameter, can have a significant effect on the change in efficiency if a different parameter has already been optimized. However, there may be little to no noticeable change if this has not yet occurred. The graphs below were modeled by a Solar Cell Capacitance Simulator (SCAPS). For further information regarding this program, see section 4.5.
Figure 3-1 shows the effect of changing the defect density within the $p$-type layer of the stack, which directly changes the carrier lifetime by the same order of magnitude. For the SnS stack, a defect density of $10^{17}$ cm$^{-3}$ corresponds to a lifetime of 0.1 ns, while a defect density of $10^{12}$ cm$^{-3}$ corresponds to a lifetime of 10 µs [13].

Typical good lifetimes for solar cells are around the 100 ns range, so a defect density for this simulation of $10^{14}$ cm$^{-3}$. The blue curve is after several other parameters in the cell have been optimized to achieve an efficiency of 16.64%. Maximum theoretical efficiencies for SnS cells are around 30%, but even in simulation, they can be difficult to achieve.
While both curves show a general trend of increased efficiency for increased lifetime, it is clear that the efficiency increases strongly with small improvements when the material starts with more defects. Eventually, the curve appears to level out, showing either that it is acceptable to have a fairly impure material with optimum performance, or the lifetime has reached another barrier and cannot improve without some additional alterations of other parameters.

The change in efficiency in SnS for the optimized and non-optimized cases, respectively are $\Delta \eta_{\text{optimized}} = 6.95\%$ and $\Delta \eta_{\text{non-optimized}} = 1.38\%$.

While defects exist within the bulk of a material, any surface or interface can be thought of as one, continuous defect, due to dangling bonds. This means it has prime opportunities for recombination. The bulk and the surface can be seen as having two separate lifetimes, but for the purpose of this thesis, only the effective lifetimes will be discussed.
It is possible to decrease the recombination velocity of a surface or interface by reducing the number of dangling bonds with supplemental atoms or better lattice matching. The results of this are shown in Figure 3-2. For this parameter, $\tau_{\text{surface}}$, the bulk lifetime yields some limitations to its effect on efficiency. For SnS, $\Delta \eta_{t=0.1ns} = 1.94\%$ and $\Delta \eta_{t=100ns} = 4.25\%$.

3.3 Introduction to Photoconductivity

The photoconductivity of a material is the effect of increased bulk conductivity due to the introduction of photons into the material. Each photon carries a specific energy dependent upon its wavelength. When the light particle reaches an electron it has the opportunity to excite the electron to the conduction band by transferring this energy. This excited electron and its corresponding hole are then free to move about the material in their respective bands, contributing to the overall conductivity. Because this is a photon-induced effect, it is called photoconductivity.

3.4 Determining the Mobility-Lifetime Product

For a material under no-light conditions, the conductivity can be modeled by:

$$\sigma_{\text{dark}} = q \ast (\mu_e n_0 + \mu_h p_0) \quad (4)$$

where, $q$ is the charge of an electron, $\mu_e$ is the mobility of an electron, $\mu_h$ the mobility of a hole, and $n_0$ and $p_0$ the intrinsic concentration of electrons and holes, respectively. For a $p$-doped material, $n_0 \ll p_0$, so the equation can be simplified to:

$$\sigma_{\text{dark}} = q\mu_h p_0 \quad (5)$$

Under illumination, carrier concentrations change with the generation of electron-hole pairs. Since each excited electron generates a hole, $\Delta n = \Delta p$:

$$\sigma_{\text{light}} = q \ast (\mu_e (n_0 + \Delta n) + \mu_h (p_0 + \Delta p)) \quad (6)$$
where $\Delta n$ and $\Delta p$ are the change in carrier concentration for electrons and holes, respectively.

From this point, two separate methods were used to calculate $\mu \tau$.

### 3.4.1 Simplified Approach

In the simplest condition, full absorption and a uniform generation is assumed over the entire volume of the sample and $\mu \tau$ is calculated from the conductivity data acquired from the experiments. The experiments were done at low injection levels and for the simplified case, generation depends only on illumination. There is neither depth nor diffusion dependence. For the change in conductivity caused by illumination:

$$\sigma_{\text{light}} - \sigma_{\text{dark}} = \Delta \sigma = q \left( \mu_e \Delta n + \mu_h \Delta p \right) \quad (7)$$

It is known that the change in charge carriers can be calculated by:

$$\Delta n = U \ast \tau = G \ast \tau \quad (8)$$

where $U$ is the recombination rate, $\tau$ is the lifetime, and $G$ is the generation rate. For the simplified case, the recombination rate is equal to the generation rate, which is calculated as the sum of all photons generated by energies above the band-gap energy on the AM1.5 spectra. Under 100% illumination of one sun, or 1000 W cm$^{-2}$, for the 1 $\mu$m thick samples, the generation rate is $2.85 \times 10^{27}$ m$^{-3}$ s$^{-1}$ for SnS and $2.08 \times 10^{27}$ m$^{-3}$ s$^{-1}$ for GaAs.

At lower illuminations, the new generation rate is simply reduced by the same fraction as the light. For example, a sample under 500 W cm$^{-2}$ illumination will observe a halved generation rate from that calculated for 1000 W cm$^{-2}$.

Combining Equations 7 and 8 yields:

$$\mu \tau = \frac{\Delta \sigma}{G \ast q} \quad (9)$$
Determining just the $\tau$ of a material is possible if $\mu$ is known, but that is beyond the scope of this thesis. The plots presented in Chapter 5 show $\mu\tau$ products acquired through the simplified approach.

### 3.4.2 Considering Non-uniform Generation

At every point within the sample, there are varying quantities of generated carriers due to the non-uniform penetration depth of photons and the diffusion of generated carriers. In this case, the depth dependence is considered, but not diffusion. This method calculates a $\mu\tau$ considering a depth and wavelength dependent generation and then uses an iterative process to individually calculate the $\mu$ and $\tau$ of the material considering the resistance acquired experimentally and bounds of $\mu$ and $\tau$ found in literature.

In the dark, the conductivity of the material doesn’t change. The dark resistance, which is related by the geometric constraints of the sample, is also constant:

$$ R_{dark} = \left( \frac{d \cdot t}{L} \cdot \sigma_{dark} \right)^{-1} = \left( \frac{q \cdot d \cdot t}{L} \cdot \mu_h \cdot p_0 \right)^{-1} \quad (10) $$

where $d$ is the length of the contacts, $L$ is the length between contacts, and $t$ is the thickness of the slab. In the light, the conductivity can now consider the depth dependence of carrier generation, as modeled by:

$$ \sigma_{light} = q \cdot (\mu_e (n_0 + \Delta n(x)) + \mu_h (p_0 + \Delta p(x))) \quad (11) $$

where $\Delta n$ and $\Delta p$ become functions of the sample depth, $x$. 

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Since the light reaches the top of the sample first, most of the higher energy photons are absorbed here. Generation decreases as the lower energy photons penetrate into the sample and interact with electrons. To model this, the sample can be split into N slabs down its thickness, shown in Figure 3-3. The generation rate becomes:

$$G(x) = \alpha \cdot N_0 \cdot e^{-\alpha \cdot x} = \frac{\Delta n(x)}{\tau}$$

(12)

where $\alpha$ is the absorption coefficient, and $N_0$ is the photon flux, found from the AM1.5 spectra. Generation rate is still equal to the recombination rate, $U(x)$, though now both are depth dependent. To model this dependence in the resistance under illumination, a summation of the resistance of each individual slab is taken:

$$\frac{1}{R_{light}} = \sum_{i=1}^{N} \frac{1}{R_i}$$

(13)

and:

$$\frac{1}{R_i} = \sigma_{light} \cdot d \cdot \frac{\xi}{L}$$

(14)

Substituting values into the $R_{light}$ equation and taking the limit as number of slabs, $N$, approaches infinity:

\[\text{Figure 3-3: Diagram of layered sample. Longer wavelength photons tend to penetrate deeper into the sample. Depth is split into } N = 5 \text{ slabs.}\]
\[ \frac{1}{R_{\text{light}}} = \int_{0}^{t} \left( \frac{d}{L} \ast q \ast ( \mu_e (n_0 + \Delta n(x)) + \mu_h (p_0 + \Delta p(x)) \right) dx \]

\[ = \frac{q \ast d}{L} \ast \left( \frac{\sigma_{\text{dark}}}{q} \ast t + \mu_e \ast \int_{0}^{t} \Delta n(x) \ dx \right) \]

\[ = \frac{q \ast d}{L} \ast \left( \frac{\sigma_{\text{dark}}}{q} \ast t + \mu_e \ast \tau \ast G \right) \]

which gives:

\[ \frac{1}{R_{\text{light}}} - \frac{1}{R_{\text{dark}}} = \frac{q \ast d}{L} \ast \mu_e \ast \tau \ast G \] (15)

therefore:

\[ \mu_e \tau = \frac{1}{R_{\text{light}}} \ast \left( \frac{1}{R_{\text{light}}} - \frac{1}{R_{\text{dark}}} \right) \] (16)

The coding process to calculate a \( \mu \tau \) product under non-uniform generation is briefly discussed in Chapter 4.4.

### 3.5 Methods of Experimental Derivation

Several methods of photoconductivity measurements currently exist which all follow the same general principles of measurement and calculation. The next sections will briefly discuss the workability and shortcomings of three methods that were considered for this thesis. Due to time constraints for both experimental work on sample fabrication and measurement as well as computational work on simulation and modeling, the simplest albeit least accurate method was chosen. These shortcomings are minor and do not significantly affect the data. The other two configurations are discussed to elaborate on the versatility of photoconductivity measurements as well as offer alternative methods for anyone hoping to take similar type measurements.
3.5.1 *Snake Configuration*

The snake configuration was a method utilized by JT Sullivan, a previous doctoral student at the MIT Photovoltaic Laboratory [9]. A schematic of his device, taken from his thesis, is shown in Figure 3-4.

![Snake Configuration Diagram](image)

**Figure 3-4**: Schematic of Snake configuration used by Joseph Timothy Sullivan. Actual samples had eight fingers. [9]

This device set-up creates a minimal spacing between contacts and minimal exposed surface area of the semiconductor material to quickly capture carriers as soon as they are generated while minimizing the effect of thermal excitation. Additional measures for preventing heating effects, such as chopping of light and a thermal sink beneath the sample, eliminates the false positives for photoconductivity associated with thermally excited carriers. The area to length ratio in this configuration is maximized to allow for very small $\Delta\sigma$ measurements.

Unfortunately, the dimensions of such a device cause it to be both difficult to fabricate and difficult to handle and measure.
3.5.2 Van der Pauw Configuration

The van der Pauw method is used to calculate the resistivity of the material, where the conductivity is the reciprocal of the resistivity. An image of possible van der Pauw configurations is shown in Figure 3-5. It is important that the sample is as symmetric as possible and the contacts are as small as possible while remaining on the edge of the sample.

![Van der Pauw Configurations](image)

**Figure 3-5**: Possible van der Pauw sheet configurations where the darker squares are the contacts. [8]

In the van der Pauw configuration, a current is run along one length of the sample while a voltage is measured across the other length. Together, these can be combined to find the resistance measurement, $R$. Assigning the contacts as 1, 2, 3, 4, starting with the upper right contact and moving clockwise on the disk configuration of Figure 3-5, if a current is run along points 1 and 2, and a voltage is measured along 3 and 4, then a resistance can be measured as:

$$R_{12,34} = \frac{V_{34}}{I_{12}}$$  \hspace{1cm} (18)

To account for asymmetric qualities of the sample, reversed polarity measurements are utilized to acquire vertical and horizontal resistances across the sample:

$$R_{\text{vertical}} = \frac{R_{12,34} + R_{34,12} + R_{21,43} + R_{43,21}}{4}$$  \hspace{1cm} (19)

$$R_{\text{horizontal}} = \frac{R_{23,41} + R_{41,23} + R_{32,14} + R_{14,32}}{4}$$  \hspace{1cm} (20)
and then substituted into the van der Pauw formula:

\[
\frac{e^{-\pi R_{\text{vertical}}/R_S}}{e^{\pi R_{\text{vertical}}/R_S}} + \frac{e^{-\pi R_{\text{horizontal}}/R_S}}{e^{\pi R_{\text{horizontal}}/R_S}} = 1 \quad (21)
\]

where \( R_S \) is the sheet resistance of the material.

Initial test measurements were taken on samples of this configuration but acquiring a \( \mu \tau \) beyond the simplified case of generation would have required modeling in 3D. None of this initial data is presented in this thesis.

### 3.5.3 Bar Configuration

All samples in this thesis are in the bar configuration. Dimensions are shown in Figure 3-6. This is the simplest method examined for measuring photoconductivity and can be modeled as a 1D or 2D problem. Electrons and holes conduct across the material as a sheet between the two contacts and the depth of the sample can be approximated as individual layers to account for the depth dependence of generation. Additionally, contacts in this configuration are easy to fabricate.

**Figure 3-6:** Bar configurations and dimensions used for experiments. GaAs is in the two-bar configuration (left) and SnS in the four-bar configuration (right).
The four-probe sample set-up is preferred because it eliminates the resistive contribution of the interface between the sample and the contact, as well as the interface between the contact and the conducting wires for measurement. In the two-bar configuration, four conducting wires are utilized, so that the latter interface contribution is still eliminated, but the resistive barrier between the contact and the sample still contributes. Even so, this contribution is very small and likely does not affect the data in this work.

Chapter 4. Experimental Procedures

4.1 Cryostat Tool

All measurements were done on an optics table using an ARS cryostat tool with NesLab chiller and a Newport LCS-100 lamp. The light intensity of the lamp was found to be 1250 W cm\(^{-2}\) as calibrated from a Si calibration sample. The measured photocurrent can be found in Figure A-1 the appendix. Two Thorlabs FW102C filter wheels are able to reduce the optical density down to 0.02% of the original light source. The set-up can be seen in Figure 4-1.

The cryostat tool is capable of reducing the temperature within the chamber to around 9 K and the temperature of the sample mounted in the chamber to around 100 K. A full cool-down requires around one hour. Precise temperatures are acquired with a feedback loop between the LabView program and a Lakeshore temperature controller. The chamber is heated using a resister coil.

There are two temperature sensors used for readings: temperature sensor A, which is placed on the central finger within the chamber and temperature sensor B, which is placed directly on the sample with a small amount of vacuum grease and an electrically and thermally isolated copper prong to hold it in place.
4.2 Sample Fabrication

The sample stack for the GaAs sample is GaAs wafer / insulating layer (MOVCD) / p-GaInP / GaAs film / p-GaInP / (Ti/Au) contact. The p-GaInP barriers passivize the surface of GaAs to reduce surface recombination effects but otherwise do not contribute to the performance of the material. The film is 1 μm thick, with contact lengths of 10.4 mm and distance between contacts measured at 13 mm. A schematic can be seen in Figure 3-6. GaAs is a direct band-gap semiconductor of 1.42 eV. In the literature, μτ values are found to be on the order of $10^{-4}$ cm$^2$ V$^{-1}$ for un-doped GaAs [3] and $1.3 \times 10^{-6}$ cm$^2$ V$^{-1}$ for p-doped GaAs at a carrier concentration of $5 \times 10^{18}$ cm$^{-3}$ [11]. The GaAs sample used in this work is highly doped up to $10^{18}$ cm$^{-3}$.
For the SnS samples, both are 1 µm thick with a contact length of 7.22 mm and a distance between contacts of 750 µm, shown in Figure 3-6. The stack is; Si substrate / insulating layer (SiO₂) / SnS / (Ti/Au) contact, where the SnS layer was deposited by thermal evaporation. SnS has both a direct and indirect band-gap of 1.3 eV and 1.1 eV respectively. Literature values of µτ for SnS did not exceed 10⁻⁷ cm² V⁻¹ [4] [22]. The annealing process for the doped sample was 4% hydrogen sulfide (H₂S) in nitrogen gas (N₂) for 10 minutes at around 80 Torr. Annealing a sample will increase the crystalline grain diameter; reducing the number of edge defects and effectively improving the conductivity of a material. Additionally, the S rich environment of the annealing process causes some S vacancies in the material to be filled, effectively increasing the Sn vacancies, which are acceptors in the p-type material [5]. The un-annealed sample is p-type with a carrier concentration around 10¹⁵ cm⁻³ while the annealed is 10¹⁶ cm⁻³. Future research may consider fabricating samples with passivation layers to reduce surface recombination. It is not explored in this thesis.

4.3 Mounting Samples

Samples are mounted to the sample holder with some vacuum grease on the back of the sample and held in place with a thermally and electrically isolated copper prong, as shown in Figure 4-2. Wires are carefully placed on the contacts and bonded with silver paint. The sample and mount are then moved to the cryostat, where it is screwed into the central finger. Temperature sensor B is placed directly on the sample with a small amount of vacuum grease and held in place with another thermally and electrically isolated copper prong. The wires are connected and the corresponding positions on the sample are noted. The outer canister is carefully secured and an Edwards TIC pumping station is turned on to create a vacuum environment.
4.4 Data Collection and Processing

The sample is cooled to very low temperatures and then heated incrementally by 20 K. The tolerance is 0.5 K and must be maintained for 60 s before each illumination measurement. Light hysteresis effects do not seem to be a problem, since the change in conductivity is sudden and returns to within 5% of the original value in the dark in less than 1 s. Even so, illumination measurements are done from dark to full illumination. A Keithley SourceMeter sources a voltage
across two contacts and the photoconductive response is measured. IV curves are generated with each measurement and all subsequent data is derived from these.

All data processing was done on the coding platform MatLab. The simplified approach to calculating $\mu \tau$ is taken to acquire an approximate estimate for each temperature and illumination measurement and generate the plots for the results section of this thesis. A more complex MatLab code created by a colleague considers the depth and wavelength dependence of generation, discussed in Chapter 3.2.2.

The code takes an $R_{\text{dark}}$, a $\mu \tau$ acquired through the simplified approach, and bounds for $\mu$ and $\tau$. Through an iterative process, it is able to determine a $\mu$ and a $\tau$ such that the calculated $R_{\text{light}}$ in the program equations is as close as possible to the $R_{\text{light}}$ found experimentally. For several data sets, the calculated $\mu \tau$ have been about a factor of two less than those found through the simplified modeling approach. A table of calculations can be found in Chapter 5.2.4.

Since the values for $\mu \tau$ acquired through the two methods correlate strongly and because the more complex approach requires each measurement be calculated separately, in the interest of time all graphs were created with $\mu \tau$ values from the simplified approach.

4.5 Solar Cell Capacitance Simulator (SCAPS):

The program used for beginning research in this work was the Solar Cell Capacitance Simulator (SCAPS), which is available, free of cost, on the web. It is “a one dimensional solar cell simulation program developed at the Department of Electronics and Information Systems (ELIS) of the University of Gent, Belgium” [24]. Through this program, a photovoltaic researcher is able to upload material properties and generate layers of a cell to simulate a $p-n$ junction. Material parameters and device properties can be set and manipulated within each layer
as well as at all interfaces. Through SCAPS, an SnS solar cell with an $n$-type layer of zinc oxy-sulfide (Zn(O,S)) was analyzed.

![Figure 4-3: Main screen of operation in SCAPS program. Simulation parameters can be inputted, such as; operating voltage, generated graphs, or saved folder location.](image)

While certain qualities, such as a thin $n$-type layer, high doping concentrations, and a low defect density, positively contributed to an increasing efficiency, it is important to note, that any quality could be impossible to achieve in the laboratory. For example, very thin layers may be impossible to fabricate, or a doping concentration that is too high will destroy the charge barrier across a $p$-$n$ junction.
For many material applications, it is most desirable to work with a pure material, where there are little to no defects. For photovoltaic research, this translates into little to no traps or recombination sites for carriers.

Figure 4-4: Main screen of SnS layer in SCAPS program. Previously loaded characteristics of the material layer can be individually edited.

Figure 4-5: Main screen for the loaded cell. A 1D depiction of the cell is given on the right. Each individual layer and interface can be altered, including the front and back contacts.
Within the SCAPS program, defects can be created and altered at each editable position to simulate this characteristic of the material. Through these defects, the lifetimes of electrons and holes can be manipulated, together or independently.

![SCAPS 3.3.02 Defect Properties Panel](image)

**Figure 4-6:** Screen of defect one of SnS layer. Characteristics specific to this defect can be edited. Changing “Nt total (1/cm3)” directly alters both carrier lifetimes equally. This effect can be seen on the main screen for the layer, represented in Figure 4-4, above. To change the carrier lifetimes separately, capture cross section can be edited.

Unfortunately, determining the most ideal qualities and quantities on SCAPS does not guarantee the perfect solar cell. While some parameters may be difficult to fabricate, other factors may hinder experimental findings, such as the interactions between two materials during deposition or strong tunneling effects at contacts. It becomes necessary to input more layers or
generate more defects within the simulation to create a more accurate image of real-life results. For example, Figure 4-5 shows a layer of ZnO between the Zn(O,S) and indium tin oxide (ITO) layers, because it forms naturally to create a stable interface.

**Chapter 5. Results**

**5.1 Test Sample GaAs**

To assess the reliability of our photoconductivity measurements, a GaAs thin-film sample was tested due to the well-known photoconductivity and mobility-lifetime values in literature. Undoped GaAs has a $\mu \tau$ on the order of $10^{-4}$ cm$^2$ V$^{-1}$ [3]. Doped GaAs with $p$-type carrier concentration on the order of $10^{18}$ cm$^{-3}$ has a $\mu \tau$ value of $10^{-6}$ cm$^2$ V$^{-1}$ [11]. The experiments, however, found the GaAs sample to have a $\mu \tau$ product three to four orders of magnitude higher, as shown in Figure 5-1.

\[ \text{Figure 5-1: } \mu \tau \text{ vs. Illumination } \% \text{ of one sun for GaAs sample.} \]
The GaAs $\mu\tau$ values show a general increase for an increase in temperature, but a
decrease for increasing illumination. The latter trend appears as $\Delta \sigma$ does not drop as quickly as
the generation rate at lower illumination values.

Additionally, for GaAs a conductivity floor exists around $3 \times 10^3 \, \Omega^{-1} \, m^{-1}$, where the
number of photo-generated carriers does not exceed the number of intrinsic carriers. Figure 5-2
shows an experimentally obtained curve comparable to the generic semiconductor carrier
generation curve, where a “freeze-out” occurs at lower temperatures, an “extrinsic region” occurs
around the flat, middle part, and an “intrinsic region” begins at high temperatures. While the
graph may be showing a freeze out at lower temperatures, the increase in conductivity near 300
K is not caused by intrinsic carriers, as this typically happened around 600 K. Instead, this may
be due to another dopant level, which becomes more accessible at higher temperatures. Data for
$\sigma$ and $\mu\tau$ for GaAs can be found in the appendix.

![Figure 5-2: Log scale of the Conductivity vs. Temperature for GaAs sample. The missing data points for the 61% and 112% curves were caused by a data collection error in the Keithley SourceMeter.](image-url)
5.2 Tin Monosulfide (SnS)

The main purpose of this thesis is to determine the \( \mu \tau \) of SnS and assess the technique and reliability of the characterization tool used to acquire it.

5.2.1 Tests for sub-band-gap Light

Initial measurements of SnS samples showed higher conductivity than anticipated. In case this was a result of sub-band-gap light exciting electrons to or from defects states within the band-gap, multiple filters were tested. Figure 5-3 shows the results of this data.

![Figure 5-3](image)

**Figure 5-3**: Log scale of the change in conductivity vs. linear scale of illumination for three different filters and the regular filters for the set-up. Notice how below band-gap light, represented by the 1250 nm long pass filter, does not offer a significant conductivity contribution. All measurements were done on the SnS annealed sample.

The direct band-gap of SnS is around 1.1 eV, which corresponds to 1127 nm wavelength light. The long pass filter at 610 nm wavelength let in much of the above band-gap light and shows nearly the same conductivity as the unfiltered light. Similarly, the band pass filter between 315 nm and 710 nm showed only a slightly lower conductivity, as expected. The long pass filter
at 1250 nm did show an increase in conductivity. However, over all illuminations, this increase was not more than 0.5 Ω⁻¹m⁻¹, which suggests that unfiltered photoconductivity is most likely due to above-band-gap excitation.

The tests for sub-band-gap light showed that lower energy excitation is not a significant problem for the conductivity measurements performed on this tool.

### 5.2.2 Noise Floor

In order to understand the sensitivity of the set-up, a noise floor was established. Multiple dark measurements were taken at 290 K on the annealed SnS sample. Conductivity was measured at 7.11 ± 0.106 Ω⁻¹m⁻¹. Several of the measurements at lower illuminations show a ∆σ value within this error range and such, cannot be trusted as accurate data. They have been omitted from the work presented in this thesis.

### 5.2.3 Effects of Annealing

For both SnS samples, μτ values were mostly on the order of 10⁻⁴ cm² V⁻¹, which is around three orders of magnitude larger than what was found in the literature. Compared to each other, the μτ values for the annealed and un-annealed SnS samples differ by about a factor of two, where the annealed sample shows larger μτ values.

The annealing process for the SnS sample both fills S vacancies and causes grain growth in the film. Reduced defect density will lead to an increase in the carrier lifetimes. S vacancies in particular are known to trap majority-carrier holes and catalyze recombination in SnS [5].

All trends for μτ calculations are similar to those found for GaAs. The μτ increases for an increasing temperature and a decreasing illumination. Data for μτ and σ for both samples can be found in the appendix.
5.2.4 Depth and Wavelength Dependent Generation

As mentioned before, two processes were used to determine the $\mu\tau$ for the samples: a simplified approach assuming uniform generation throughout the thickness of the material and a more complex modeling of the depth and wavelength dependence of charge carrier generation. Table 5-1 shows the results of this dependence compared to the simplified approach for a few temperatures at 1120 W cm$^{-2}$ illumination.

Table 5-1: Data set of $\mu\tau$, fitted $\mu$, and fitted $\tau$ values for all three samples at temperatures from 230 K to 310 K. Values of $\mu\tau$ calculated from the uniform generation method and depth and wavelength dependent generation method are about a factor of two different from each other. The fitted $\mu$ and fitted $\tau$ values are not exact. Repeating calculations can cause the fitted values to change by an order of magnitude, but their product will always be nearly exactly that of the calculated $\mu\tau$ value in the case for non-uniform generation.

<table>
<thead>
<tr>
<th>GaAs</th>
<th>Temperature [K]</th>
<th>230</th>
<th>250</th>
<th>270</th>
<th>290</th>
<th>310</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu\tau$ at Uniform Generation</td>
<td>2.84E-01</td>
<td>2.93E-01</td>
<td>2.95E-01</td>
<td>2.95E-01</td>
<td>2.84E-01</td>
<td></td>
</tr>
<tr>
<td>$\mu\tau$ at Non-uniform Generation</td>
<td>6.84E-01</td>
<td>7.03E-01</td>
<td>7.08E-01</td>
<td>7.09E-01</td>
<td>6.82E-01</td>
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<tr>
<td>$\mu$ Fit</td>
<td>9.30E+01</td>
<td>7.90E+01</td>
<td>7.20E+01</td>
<td>7.70E+01</td>
<td>7.70E+01</td>
<td></td>
</tr>
<tr>
<td>$\tau$ Fit</td>
<td>7.30E-03</td>
<td>9.00E-03</td>
<td>9.90E-03</td>
<td>9.30E-03</td>
<td>8.80E-03</td>
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</table>

<table>
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<th>Temperature [K]</th>
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<th>250</th>
<th>270</th>
<th>290</th>
<th>310</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu\tau$ at Uniform Generation</td>
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<td>3.22E-05</td>
<td>4.61E-05</td>
<td>5.42E-05</td>
<td>6.19E-05</td>
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<tr>
<td>$\mu\tau$ at Non-uniform Generation</td>
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<td>7.74E-05</td>
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<td>1.30E-04</td>
<td>1.49E-04</td>
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<tr>
<td>$\mu$ Fit</td>
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<td>4.07E+00</td>
<td>2.81E+00</td>
<td>9.00E-01</td>
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<tr>
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<td>4.64E-05</td>
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<table>
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<th>250</th>
<th>270</th>
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<th>310</th>
</tr>
</thead>
<tbody>
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<td>$\mu\tau$ at Uniform Generation</td>
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<td>2.29E-04</td>
<td>2.27E-04</td>
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<tr>
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</table>

The values calculated by including the depth and wavelength dependent generation are about a factor of two higher than those calculated assuming uniform generation. This makes sense, because the integrated non-generation is smaller than the uniform generation case and since generation is in the denominator for determining $\mu\tau$, Equation 9 in Chapter 3.4.1, $\mu\tau$ will be higher.
Since the non-uniform generation is calculated with an integral, the $\mu \tau$ values generated are strongly dependent upon the discretization used. For example, if the number of discrete layers, $N$ is set to 100, this gives a layer thickness of 10 nm. Due to the exponential dependence of generation, Equation 12 in Chapter 3.4.2, the surface of the material will generate several times more, even several orders of magnitude more, charge carriers than further down into the sample. For this reason, initial calculations at $N = 100$ overestimated generation and therefore underestimated $\mu \tau$ to be less than that calculated in the simplified case. The influence of $N$ on $\mu \tau$ calculations can be seen in Figure 5-4.

![Figure 5-4](image)

**Figure 5-4:** Log scale of the number of layers modeled into which the sample is split for modeling, $N$ vs. $\mu \tau$. All values were taken at 290 K and an illumination of 1120 W cm$^{-2}$ for the GaAs sample.

As $N$ increases, the calculation of depth and wavelength dependent generation becomes more precise, similar to taking a Riemann Sum with a smaller and smaller $\Delta x$. At values around $N = 5000$, the values for $\mu \tau$ begin to plateau around $7.1 \times 10^{-1}$ cm$^2$ V$^{-1}$ for GaAs, $5.5 \times 10^{-4}$ cm$^2$ V$^{-1}$
for the annealed SnS, and $1.3 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1}$ for the un-annealed SnS sample. At $N = 5000$, layer thickness is around 2 Å. Additionally, this shows the incredible influence of surface defects. At the atomic scale, just the first 10 nm accounts for more than 95% of overall generation. If the defect density at the surface of the material is large, most of these generated carriers will be lost.

### 5.2.5 Low illumination measurements

For the annealed SnS sample, the conductivity at lower illumination values was higher than expected, while at very high illumination values, the conductivity was found to be somewhat smaller than expected. This trend is similar for the un-annealed sample, although less pronounced. A plot of $\sigma$ vs. illumination for the annealed SnS sample can be seen in Figure 5-5.

![Graph](image.png)

**Figure 5-5:** Conductivity vs. Illumination for SnS annealed sample. Minimal $\Delta \sigma$ at low illumination possibly due to sensitivity of machine and unfilled traps.

At low light intensity, the conductivity of the sample becomes larger very rapidly but then transitions into an almost linear region. This could be due to the sensitivity of the instruments picking up a low signal. It may also be considered, that traps will have a greater
influence on conductivity at lower light intensities because there are not as many carriers available to both fill the traps and continue conducting through the material. At higher light intensities, more traps are filled, allowing other carriers to move about.

Questioning the large $\mu \tau$ produced at low illumination requires re-examining Equation 9 from section 3.2.1. While the $\Delta \sigma$ of the sample is decreasing with decreasing illumination values, it is not doing so proportional to the reduction in generation rate, which is in the denominator of this equation. The generation rate is reduced to a percent of the total generation rate equal to the illumination percent value. This can cause the denominator to become very small, while the $\Delta \sigma$ doesn’t change very much, leading to a very large $\mu \tau$. For this reason, it is better to consider $\mu \tau$ values acquired from larger light intensities, which show a linear relationship with $\sigma$.

5.2.6 Seebeck Measurements

In an effort to determine the type of carrier dominating conductivity measurements, an experiment to determine the Seebeck coefficient of the material was done. Unfortunately, this did not yield tangible results.

Samples were arranged such that one side would be heated and a temperature gradient would form. A voltage was then measured across this gradient. The sign of the measured change in voltage would determine the dominant carrier type. Unfortunately, the measured $\Delta V$ values were too small to overcome the noise of the experiment.

A typical Seebeck measurement is on the range of 100 $\mu V K^{-1}$, therefore the temperature gradient across the sample would need to be several K in order to acquire a good signal. The length across the sample is only 8.6 mm, so acquiring a several K difference would be very difficult, especially considering that the Si substrate of the film is a fairly thermally conductive
material. It is likely that the thermal conduction was through the substrate rather than the film itself, making a Seebeck measurement difficult.

Further experimentation on this tool would benefit greatly from a successful Seebeck measurement or if possible, a Hall measurement, to determine the dominant charge contribution to the measured conductivity values.

Chapter 6. Conclusions

6.1 Discussion and Impact

These experiments have yielded a much higher $\mu \tau$ product than anticipated, on the order of three to four orders of magnitude higher for all three samples. There could be a number of factors contributing to this, but ultimately, it is believed that this measurement technique is showing a majority-carrier $\mu \tau$.

The calculations done considering depth and wavelength dependent charge carrier generation have yielded results only about a factor of two different than those found using a simplified approach. Additionally, the code is not too computationally intensive; several thousand layers can be modeled in seconds. The depth and wavelength dependent generation offers more precise measurements for $\mu \tau$, but uniform generation still yields reasonable results.

6.1.1 Doping Effects

Originally, it was expected that the measured change in carrier concentrations for holes and electrons would be equal and that the doping of the sample would not have a significant effect on the measured values using this method. This is not the case. Doping has had a notable effect, particularly in the GaAs sample.
Typically, as a material becomes more doped, the carrier mobility decreases [12]. In the case of literature values of the $\mu\tau$ for GaAs, heavily doping the material can decreases the $\mu\tau$ by two orders of magnitude. This is likely also due to an increased chance of recombination and resulting shorter lifetime for minority-carriers. A strong argument that the methods discussed in this thesis measure the majority-carrier is the measured $\mu\tau$ values for GaAs.

In a GaAs sample doped up to $10^{18}$ cm$^{-3}$, $\mu_n = 1.1 \times 10^3$ cm$^2$ V$^{-1}$ s$^{-1}$ [12], $\mu_p = 1.8 \times 10^2$ cm$^2$ V$^{-1}$ s$^{-1}$ [12] and $\tau_n = 1.2 \times 10^{-9}$ s [11]. Values for $\tau_n$ were assumed to equal $\tau_p$. With these measurements, a doped GaAs sample would need a value of $\tau_p = 1.57 \times 10^{-3}$ s to acquire the measured $\mu_p \tau_p = 2.8 \times 10^{-1}$ cm$^2$ V$^{-1}$ at 1120 W cm$^{-2}$ illumination and 310 K. It is likely that while the increased chance of recombination due to the increased number of holes significantly reduces the minority-carrier lifetime, the majority-carrier lifetime could actually increase because so many of the carriers will not be recombined and will instead be collected by the contacts.

The SnS samples are doped two to three orders of magnitude less than the GaAs samples. However, the effect on $\mu\tau$ is the opposite case when they are compared with each other. The annealed SnS sample is doped an order of magnitude more than the un-annealed sample and this leads to a factor of two increase in $\mu\tau$. This improvement may just be a result of reduced bulk defects by annealing.

### 6.1.2 Variations from Literature Data

From the literature, $\mu\tau$ products for SnS not greater than $10^{-7}$ cm$^2$ V$^{-1}$ were acquired from two different techniques: a similar photoconductivity measurement to the one discussed in this work of sourcing a voltage and measuring the photoconductive response of extended light pulses [4] and an optical pump, terahertz-probe photoconductivity (TPC) measurement [22]. For the latter technique, TPC, it is known that the minority charge carrier was dominating $\mu\tau$
measurements and that the measured SnS samples were grown and processed using the same methods as this work. The former technique was performed on cubic-crystalline SnS with a band-gap of 1.7 eV, while the films in this work and for the TPC measurements have an orthorhombic crystalline structure. Additionally, the SnS films with the cubic-crystalline structure were grown in a chemical bath and likely had much smaller grains, contributing to higher recombination rates and a lower $\mu\tau$.

For both SnS samples, the effects of doping are not likely to be the cause of such a significant difference between the $\tau_n$ and $\tau_p$. Determining what has caused this disparity is beyond the scope of this thesis, though it may be linked to a recombination-active defect present in the material. Currently, very little is known about defects in SnS specific to recombination.

### 6.2 Further Research

Further research suggestions would explore varying annealing parameters, doping levels, and growth techniques of SnS films. An undoped GaAs sample could be tested on the tool and compared with recorded literature values to further assure the quality of data collected. Additionally, a successful Seebeck coefficient or Hall measurement would determine the dominant contributing carrier to photoconductivity and confirm that the majority-carrier yields the results presented in this thesis.
Bibliography


Figure A-1: Calibrated photocurrent in Suns with Si calibration sample on a log scale. The light intensity of the Newport LCS-100 lamp used for the experiments was found to be 1250 W cm$^{-2}$. Filter wheel #1 is capable of attenuating light by an optical density of 0.1, 0.2, 0.3, 0.4, and 0.6. Filter wheel #2 can do 0.5, 1.0, 2.0, 3.0, and 4.0. The two filter wheels could combine any set of filters to attenuate from an optical density from 0 to 4.6.
Table A-1. Values for $\sigma$ calculated using the uniform-generation approach. Missing values are a result of a momentary data collection error in the Keithley SourceMeter during measurements. No or incomplete data was taken.

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<th>GaAs</th>
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| SnS un-annealed | Illumination [% of one Sun] |
|                 | Temperature [K]              |
|                 | 0   | 0.289 | 1.81 | 9.67 | 29.6 | 112 |
| 210             | -   | -    | 4.26E+00 | 5.26E+00 | 7.30E+00 | 1.14E+01 |
| 230             | 1.03E+00 | 3.81E+00 | 4.18E+00 | 6.44E+00 | -   | -    |
| 250             | 3.04E+00 | -    | -    | 9.06E+00 | 1.19E+01 | 1.75E+01 |
| 270             | 4.17E+00 | 7.55E+00 | 1.03E+01 | 1.42E+01 | 1.80E+01 | 2.49E+01 |
| 290             | 8.09E+00 | 1.19E+01 | 1.52E+01 | 1.99E+01 | 2.43E+01 | 3.24E+01 |
| 310             | 1.53E+01 | 1.92E+01 | 2.30E+01 | 2.85E+01 | 3.38E+01 | 4.31E+01 |

| SnS annealed | Illumination [% of one Sun] |
|             | Temperature [K]              |
|             | 0   | 0.289 | 1.81 | 9.67 | 50.6 | 112 |
| 130           | 1.52E+01 | 2.38E+01 | 4.00E+01 | 6.47E+01 | 1.03E+02 | 1.28E+02 |
| 150           | 1.40E+01 | 2.12E+01 | 3.47E+01 | 5.47E+01 | 8.60E+01 | 1.08E+02 |
| 170           | 1.49E+01 | 2.20E+01 | -    | 5.25E+01 | 8.11E+01 | 1.01E+02 |
| 190           | 1.76E+01 | 2.48E+01 | -    | 5.52E+01 | 8.32E+01 | 1.03E+02 |
| 210           | 2.24E+01 | 3.04E+01 | 4.35E+01 | 6.23E+01 | 9.09E+01 | 1.11E+02 |
| 230           | 3.03E+01 | 3.91E+01 | 5.33E+01 | 7.32E+01 | 1.03E+02 | 1.24E+02 |
| 250           | 4.25E+01 | 5.20E+01 | 6.72E+01 | 8.84E+01 | 1.20E+02 | 1.42E+02 |
| 270           | 6.26E+01 | 7.23E+01 | 8.80E+01 | 1.10E+02 | 1.43E+02 | 1.65E+02 |
| 290           | 9.49E+01 | 1.04E+02 | 1.19E+02 | 1.41E+02 | 1.74E+02 | 1.97E+02 |
| 310           | 1.44E+02 | 1.51E+02 | 1.64E+02 | 1.84E+02 | 2.16E+02 | 2.39E+02 |
Table A-2. Values for $\mu t$ calculated using the uniform-generation approach. Missing values are a result of a momentary data collection error in the Keithley SourceMeter during measurements. No or incomplete data was taken.

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