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DETECTION OF EFFICIENCY-LIMITING DEFECTS IN CADMIUM TELLURIDE

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ABSTRACT

Cadmium telluride is one of the leading materials in thin-film solar cell technologies. CdTe solar cells have one of the highest theoretical efficiencies of all materials. However, efficiencies are currently limited due to deep-level defects acting as recombination centers. It is currently not well understood how the properties of different dopants contribute to the introduction of new defects or augmentation of existing intrinsic defects. In this study, Electron Paramagnetic Resonance (EPR) is used to characterize the defects present in undoped, *p*-type, and *n*-type CdTe. The differences in the EPR spectra for differently doped samples provides evidence that particular dopants may not be well suited for solar cell applications. Most notably, EPR signals in As-doped CdTe may have indicated a significant concentration of tellurium vacancies, which may act as efficiency-limiting recombination centers in solar cell applications due to their energy level near the center of the CdTe band gap.

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Chapter 1

Introduction

1.1) Motivation

Cadmium telluride (CdTe) is a material of great interest due to its potential for use in high-efficiency thin film solar cells [1]. CdTe is one of the most widely used materials for solar cell applications, second only to silicon [2]. Although CdTe trails silicon in terms of solar cell efficiency, solar cell manufacturers project considerable gains for CdTe cells in the coming years [3]. However, these improvements will depend on a determination of the current limitations of CdTe [1]. Identification of the ideal dopant will be an important step in this process. However, it is known that the properties of certain dopants may have a detrimental effect on cell efficiency due to the introduction of deep-level defects [4]. Therefore, there is great incentive to fully characterize the deep-level defects the may be present in doped CdTe.

1.2) Problem Statement

Electron Paramagnetic Resonance (EPR) is the most powerful analytic tool for the identification of defects in semiconducting materials [5]. In this experiment, EPR will be utilized in an attempt to identify defects in a variety of *n*-type, *p*-type, and intrinsic CdTe samples. The samples under analysis were all grown using the same techniques, with the dopant type being the only variable. This allows for the controlled study of how a specific dopant might positively or negatively impact solar cell efficiency. Although there have been numerous studies involving the

characterization of CdTe crystals by EPR, little is known about the effects of these specific dopants on the creation of additional defects. Comparison of EPR spectra obtained for each of these samples will allow us to determine whether some defects are unique to crystals of a certain doping type. The defects of greatest interest are those that may act as efficiency-limiting recombination centers in solar cells.

Chapter 2

Background and Literature Review

An understanding of what is and is not desirable in solar cell materials is reliant on a basic understanding of how solar cells operate under normal conditions. However, given that a simple single-junction solar cell is a specific application of a p-n junction, it is first necessary to summarize the essential physical details of how a p-n junction operates.

2.1) Basic semiconductor physics and the *p*-*n* junction

Although the CdTe/CdS heterojunction that is relevant to this study is more complex, it is instructive to consider the physical details of a simple *p*-*n* homojunction. Consider a pure semiconductor crystal. For the sake of example, let us take the crystal to be silicon (Si). At 0K, all of the bonding electrons between the Si atoms are held within the bonds as part of what is called the valence band [6]. However, as energy is added to the system, some electrons gain sufficient energy to leave their bonds and enter the conduction band, at which point the electron is free to travel throughout the crystal and carry a current [6]. When this occurs, the electron leaves an unoccupied electron state behind in the valence band. A different electron in the valence band can shift to fill this empty state, leaving behind an empty state. In this way, there is effectively a positive charge traveling through the crystal, which is referred to as a hole [6]. There exists a range of energies between the valence and conduction bands for which occupation is forbidden, a result of quantum mechanics [6]. This energy range is referred to as the "bandgap" of the material, and is typically on the order of 1 eV for semiconductors [6].

Although the valence and conduction bands are typically viewed as continuous energy ranges, they actually consist of discrete, very energetically close allowed energy states [6]. The distribution of these energy states as function of energy is described by the density of states. The effective density of states at the bottom of the conduction band is given by

$$N_C = 2\left(\frac{2\pi m_e^* kT}{h^2}\right)^{3/2} \tag{1}$$

where m_e^* is the effective electron mass, k is the Boltzmann constant and h is Planck's constant [6]. Similarly, the effective density of states at the top of the valence band is given by

$$N_{\nu} = 2 \left(\frac{2\pi m_{h}^{*} kT}{h^{2}}\right)^{3/2}$$
(2)

where m_h^* is the effective hole mass [6].

Additionally, the probability that a given electron state is occupied is described by the Fermi-Dirac function,

$$f(E) = \exp\left[-\frac{E - E_F}{kT}\right]$$
(3)

where E_F is the Fermi energy [6]. The Fermi energy is the energy at which the probability of occupation is one half [6]. However, since this energy always lies between the conduction and valence bands, an electron cannot actually exist at this energy.

Combining the Fermi-Dirac function with the expressions for N_c and N_v , we can develop expressions which give us the concentrations electrons at the bottom of the conduction band and holes at the top of the valence band. These expressions are given in Equations (4) and (5), respectively:

$$n = N_c \exp\left[-\frac{(E_c - E_F)}{kT}\right] \tag{4}$$

$$p = N_{v} \exp\left[-\frac{(E_{F} - E_{v})}{kT}\right]$$
(5)

Now let us consider the addition of impurity atoms to the silicon crystal. If some of the silicon atoms in a crystal are replaced with atoms with one extra valence electron, very little energy is needed for the impurity atom to ionize and for the extra electron to enter the conduction band. This is referred to as n-type doping. Conversely, if the impurity atoms have one less valence electron than silicon, they will essentially be contributing a hole to the valence band. This is referred to as p-type doping. The addition of n- or p-type dopants can dramatically increase the concentrations of electrons in the conduction band or holes in the valence band, respectively.

At this point, we can consider the p-n junction. Consider a piece of n-type silicon that is joined together with a piece of p-type silicon. Because the Fermi energy of a material must be uniform throughout at equilibrium [6], there must be a difference in the conduction band and valence band energies from one side of the junction to the other. This is depicted in Figure 1.



Figure 1: Schematic of a p-n junction at equilibrium [7]

Due to the high concentration of electrons in the conduction band of the *n*-side, electrons will tend to diffuse into the *p*-side, leaving behind positively charged ion cores from the *n*-type dopants atoms. Likewise, holes will diffuse from the *p*-side to the *n*-side, leaving behind

negatively charged ion cores. Eventually, these ion cores will establish an opposing electric field at and around the junction which is sufficient to prevent further diffusion of electrons and holes. At this point, there is a region at the center of the junction that is depleted of holes and electrons, appropriately referred to as the depletion region [6]. The corresponding voltage across this region is referred to as the built-in voltage [6].

Finally, we must consider this p-n junction when there is an applied voltage (bias). When a positive voltage is applied from p-side to n-side, this voltage can oppose the built-in voltage, effectively reducing the energy barrier that is preventing further diffusion of electrons and holes across the depletion region. This is the "forward biased" mode of operation, and results in a diffusion current. If the opposite polarity voltage (reverse bias) is applied across the junction, the energy barrier increases and the only current is a result of the relatively few conduction electrons on the p-side flowing to the n-side (and few holes in the p-side flowing to the n-side.)

2.2) Basic solar cell operation

It was previously stated that a solar cell is simply a p-n junction operating under specific conditions. Again, let it be emphasized that there are some major practical differences between the CdTe/CdS heterojunction solar cell and the simple p-n homojunction solar cell discussed here. However, an analysis of this simpler model is sufficient for demonstrating the implications of deep-level defects in solar cell materials, since the same physical principles apply in both cases.

Consider what occurs when a p-n junction is placed under electromagnetic radiation. If an incident photon has sufficient energy, it can promote an electron from the valence band to the conduction band, leaving a hole in the valence band [1]. If this electron-hole pair is formed in the

n-type region, the relative increase in concentration of electrons in the conduction band is negligible, given that there is already a high concentration of conduction electrons due to the doping with donor atoms. However, there is a very low concentration of holes in the valence band on the *n*-side, so the addition of holes due to electron-hole pair generation causes a significant increase in hole concentration. Conversely, on the *p*-side, electron-hole pair generation due to irradiation causes a negligible increase in hole concentration in the valence band, but a significant increase in electron concentration in the valence band. The implications of these changes in electron and hole concentrations are dependent on the region in which the electron-hole pairs are generated [1].

Consider the generation of an electron-hole pair the depletion region. Due to the built-in voltage across the depletion region, the generated electron will drift to the *n*-side and the generated hole will drift to the *p*-side, where they are majority carriers. Thus, there is a net flow of charge – the photocurrent. In this way, energy from incident electromagnetic radiation has effectively been converted into electrical energy that can be used to do work.

Now, consider an electron-hole pair that is generated in the bulk of the *p*-type semiconductor. As was previously discussed, this generation only results in a significant increase in electron concentration. In order for this electron to contribute to the photocurrent, it must reach the depletion region and flow to the *n*-side. However, the fact that the electron is a minority carrier complicates this process. The electron will only exist for a certain amount of time in the *p*-side before it meets a hole and recombines, eliminating its potential to contribute to the photocurrent. This amount of time is referred to as the carrier lifetime (τ) and is dependent on the type and quality of material being used, as well as dopant concentrations [1]. The distance that this electron can diffuse during its lifetime is given by the diffusion length,

$$L = \sqrt{D\tau} \tag{6}$$

8

where D is the diffusion constant of the electron, which is also material-dependent [1]. Therefore, if the electron-hole pair is generated more than one diffusion length from the depletion region, the electron is likely to recombine before it can reach the depletion region. However, if the pair is generated within one diffusion length from the depletion region, the electron has a higher probability of reaching the depletion region, contributing to the photocurrent. The same arguments could be made for holes generated in the *n*-region. This qualitative discussion of photocurrent generation in a *p*-*n* junction solar cell can be visualized in Figure 2.



Figure 2: Charge carrier generation and diffusion in a p-n junction solar cell [1]

2.2.1) Solar cell design considerations

In principle, photocurrent can be generated by both the electrons generated in the p-side and holes generated in the n-side. However, the mobility of electrons in a semiconductor is generally much greater than the mobility of holes. This is of great importance in the context of solar cells, because a higher mobility leads to a higher diffusion length. Therefore, it is optimal to have the majority of light absorption occur in the p-side of the solar cell. For this reason, the typical solar cell consists of a relatively thin n-side and a thicker p-side. This is demonstrated in Figure 3.



Figure 3: Generic p-n junction solar cell design [1]

Figure 3 also depicts the light as incident on the thin *n*-side. If the *n*-side is thin enough, the majority of incident photons will be able to penetrate to the *p*-side before they are absorbed. It is helpful to consider a quantitative description of absorbance in semiconductors.

A photon of frequency v has energy $E_{ph} = hv$. If E_{ph} is greater than the bandgap E_G , the photon will be absorbed, promoting an electron from the valence band into the conduction band. However, any excess photon energy beyond the bandgap energy (that is, the difference $E_{ph} - E_G$) will be lost to lattice vibrations [1]. Photons with $E_{ph} < E_G$ cannot be absorbed by the semiconductor, and therefore cannot contribute towards generating a photocurrent.

Consider a particular wavelength of light incident on a solar cell with intensity *I*_o. As the light penetrates the solar cell, some photons will be absorbed, leading to an exponential decay in intensity. The decrease in intensity of the light as a function of the depth passed into the solar cell is given by the Beer-Lambert law:

$$I(x) = I_o \exp(-\alpha x) \tag{7}$$

10

Here, α is the absorption coefficient, typically given in units of (cm⁻¹). α is inversely related to photon wavelength and is dependent on the specific material being used [1]. Values of α as a function of photon energy for some common semiconducting materials are shown below in Figure 4.



Figure 4: Absorbance curves for various semiconductors [1]

It is clear from the Beer-Lambert law that a higher value of α (which implies higher photon energy/lower photon wavelength) leads to a more rapid decay of light intensity, meaning that more photons are being absorbed. High-energy photons will not penetrate as deep as low energy photons before they are absorbed. This relationship is often expressed using the penetration depth

$$x_p = \frac{1}{\alpha} \tag{8}$$

which is equivalent to the depth at which the light intensity has decayed by 63% [1].

Photons with too low of an energy will not be absorbed by the solar cell. However, too high of an energy will result in the photon being absorbed in the *n*-side of the solar cell, and it was previously established that absorption in the *p*-type material is preferred. Evidently, there is a specific range of photon energies (or wavelengths, $\lambda = \frac{c}{v}$) which we are interested in for solar cell applications [1].

There is one final detail that must be considered before moving on to a discussion of the limitations of solar cells. In Figure 4, one can observe an obvious difference in the shapes of the absorbance curves between c-Si (crystalline silicon) and the other materials. This difference is a consequence of the difference between direct and indirect bandgap semiconductors. With direct bandgap semiconductors, the electron states at the top of the valence and bottom of the conduction band have different energies, but the same momentum [6]. Therefore, when an electron is excited into the conduction band, no change in momentum must occur. Some examples of direct bandgap semiconductors, electrons that are excited from the valence band to the conduction band must undergo both a change in energy and a change in momentum. This change in momentum occurs through the absorption or emission of lattice vibrations [6]. Absorption in an indirect bandgap semiconductor such as c-Si is less efficient than absorption in a direct bandgap semiconductor.

One can clearly observe this difference in absorption efficiency in Figure 4. Taking CdTe, for example, one can see that α increases rapidly for photons with energy greater than the bandgap. However, for c-Si, α increases relatively slowly, indicating that there is a wider range of photon energies for which absorption occurs at a greater penetration depth.

2.3) Current Progress with CdTe in Solar Cells

Cadmium Telluride (CdTe) is a material of great interest for solar cell applications. The reasoning for this will become clear after an in-depth consideration of solar cell efficiency. However, we will first briefly consider the design of solar cells using CdTe, as well as the performance of these devices in both laboratory and commercial contexts.

2.3.1) Typical CdTe Solar Cell Design

The basic structure of a *p*-*n* junction solar cell was depicted in Figure 3. According to the 2016 International Technology Roadmap for Photovoltaics, the average thickness of crystalline silicon *p*-*n* junction solar cells was on the order of 100 μ m, and is not projected to decrease significantly in the next decade [8]. However, due to its high absorption, CdTe (along with other direct bandgap semiconductors) can be used to manufacture solar cells of thickness on the order of 1-10 μ m [1]. These solar cells are appropriately called "thin-film" solar cells. When used in solar cells, *p*-type CdTe is typically part of a heterojunction with *n*-type CdS. A basic CdTe/CdS thin film solar cell is depicted in Figure 5.



Figure 5: CdTe/CdS thin film solar cell design [1]

Figure 5 also shows a glass superstrate and an indium-tin oxide (ITO), which is transparent and conductive [1]. One advantage of CdTe is that it can be deposited as a thin film in very high quality using thermal evaporation [1]. The growth and quality of CdTe crystals used in these cells can typically be improved by treatment with CdCl₂, although the mechanism of this improvement is poorly understood [1].

2.3.2) Performance of CdTe/CdS Solar Cells

CdTe solar cells make up approximately 5% of the worldwide solar cell market [9]. In 2016, First Solar, Inc. reported a record breaking CdTe solar cell efficiency of 22.1% [3]. Additionally, First Solar reported that the average efficiency of their commercially available CdTe based modules was 16.1% [9]. In contrast, crystalline silicon solar cells have maximum laboratory efficiencies of over 25% and commercial efficiencies ranging from 18-22% [10]. Although CdTe solar cells are significantly less efficient than current crystalline silicon cells, manufacturing companies such as First Solar project significant increases in efficiency for CdTe cells in the coming years.

2.4) Limitations of Solar Cell Efficiencies

In general, the efficiency η of a solar cell can be described by

$$\eta = \frac{P_{max}}{P_{opt}} \tag{9}$$

where P_{max} is the power output by the solar cell at its maximum power point and P_{opt} is the incident optical power [1]. An efficiency of one would imply that 100% of the incident photon energy on a solar cell is converted to usable electrical energy. However, such a situation is neither practically nor theoretically possible.

2.4.1) Theoretical limitations: The Shockley-Queisser Limit

William Shockley, known for his theoretical model of *p*-*n* junction solar cells, is also known for his assessment of the theoretical maximum efficiency of a *p*-*n* junction solar cell. Together with Hans Queisser, Shockley derived an expression for solar cell efficiency as a function of the temperatures of the sun and solar cell, the bandgap of the semiconductor being used, the probability of an incident photon generating an electron-hole pair, and several other variables [11]. The result of this mathematical analysis is referred to as the Shockley-Queisser limit. In determining this limit, the sun and the solar cell were assumed to be ideal black bodies, resulting in smooth curves for efficiency vs. bandgap energy [11]. However, a more realistic model takes into account the specific properties of the solar spectrum and light absorbance due to Earth's atmosphere [1]. This modified model yields a more irregular curve, as depicted in Figure 6. Figure 6 also illustrates the record solar cell efficiencies for different solar cell materials (as of 2016).



Figure 6: The Schockley-Queisser limit as a function of bandgap energy Eg [12]

There are several important details to note about the Shockley-Queisser limit. First, the theoretical maximum efficiency is predicted to be 33.16% at a band gap energy of 1.34 eV [12]. Note that this optimal band gap is higher than that of crystalline silicon, for which the maximum efficiency is slightly greater than 30%. Rather, this optimal band gap is close to the band gaps of

CdTe (1.44 eV), InP (1.27 eV), and GaAs (1.43 eV) [13]. Therefore, these materials are of great interest in the development of high-efficiency solar cells.

From the Shockley-Queisser limit, it is clear that the majority (67% at minimum) of light energy is not converted to usable electrical energy in a p-n junction solar cell. A large fraction of this loss can be attributed to the conversion of light energy into heat. Furthermore, a fraction of incident photons will not be absorbed by a solar cell. These losses are consequences of the properties of the solar spectrum.

If the solar spectrum consisted of only a very narrow range of wavelengths, one could simply choose a solar cell material for which absorbance is optimal at these wavelengths. However, the solar spectrum consists of a broad range of wavelengths, as shown in Figure 7.



Figure 7: Properties of the solar spectrum [1]

Clearly, the greatest electromagnetic power from the sun is at and around a wavelength of 500nm (photon energies of approximately 2.5eV). This provides a useful criterion for evaluating the effectiveness of different semiconductors in solar cells. The optimal material will have high absorbance values at these wavelengths, but not so high as to have very shallow penetration depths, as this would lead to absorbance in the *n*-side of the solar cell. Referring to Figure 4, it appears that GaAs and CdTe are two materials for which this criterion is met.

2.4.2) Practical limitations of solar cells

The Shockley-Queisser limit restricts the maximum theoretical efficiency of a p-n junction solar cell to around 33%. In practice, the theoretical limitations determined by Shockley and Queisser are far from being the only dampers on solar cell performance. As long as solar cell efficiencies remain below the theoretical limit, there is great motivation to consider the nature of these practical limitations.

As was discussed in Section 2.2, the generation of electrical current in a solar cell relies on the diffusion of photon-generated electron-hole pairs. The diffusion length of a minority carrier (Eq. 6) is dependent on lifetime of that carrier in the material. The minority carrier lifetime is the average amount of time that a minority carrier exists before recombining with a majority carrier. In situations with higher probability of recombination, the minority carrier lifetime is decreased, thus decreasing the diffusion length. The result is a decrease in the effective area over which the generation of electron-hole pairs can contribute towards generating a photocurrent.

One mechanism by which recombination can occur is through the Shockley-Read-Hall model of recombination, commonly known as trap-assisted recombination [14]. This type recombination is a consequence of empty energy states between the valence and conduction bands of a semiconductor, which act as recombination centers. Recall that, in a pure semiconductor, the energies between the valence and conduction bands are forbidden. However, imperfections in the crystal lattice (e.g. vacancies and impurities) can introduce empty energy levels in this region [6]. Consider an electron traveling in the conduction band. When this electron encounters such a defect, it may become trapped due to the resulting decrease in energy. If the energies of the trap and the conduction band are sufficiently close, the electron may be able to return to the conduction band. However, for trap energies closer to the center of the bandgap ("deep level" defects), an electron will remain trapped. If a hole in the valence band encounters this same defect, recombination will occur. This process is depicted in Figure 8.



Figure 8: The Shockley-Read-Hall model of recombination[6]

The presence of recombination centers in semiconductors is a significant limitation on solar cell efficiencies. Each material may have its own unique types of recombination centers. Let us consider those that are present in CdTe.

Metal impurities can be a major source of recombination centers in CdTe [15]. The energy levels of these metal impurities relative to the valence and conduction bands of CdTe can be seen in Figure 9.



Figure 9: Defect energy levels of metal impurities in CdTe [15]

Clearly, a large number of these metals have energy levels close to the center of the CdTe bandgap. Therefore, these impurities will be important recombination centers to consider.

Interestingly, in the study in which these impurities were examined, a high number of deep-level defects was desirable in order to increase resistivity for X-ray detection applications [15].

Intentional doping is an additional factor that can affect the efficiency of solar cells. As is the case with most semiconductor devices, solar cells rely on doping in order to achieve optimal performance. Therefore, although intrinsic CdTe will be analyzed in this experiment as well, we are primarily concerned with the properties of extrinsic CdTe. Although doping allows for high charge carrier concentrations, an improper choice of dopant can have negative consequences. In selecting the optimal dopant, one must consider many factors. For example, dopants with low solubility in the material of interest are not practical choices. It is also important to consider the donor/acceptor energy levels of the dopant atoms. For an *n*-doped semiconductor, donor levels should be close to the conduction band in order to promote ionization of the dopants. Likewise, acceptor levels in p-doped materials will ideally be close to the valence band. A third consideration in selecting a dopant is the formation of compensating defects in the crystal. Specifically, when electrically active dopants are added to a crystal lattice, the crystal will tend to lower its energy by forming defects such as vacancies and interstitials [16]. The formation of these intrinsic defects will oppose the effects of the doping. The severity of this compensation depends on the specific crystal-dopant system. It is possible for these compensation defects to act as recombination centers. Therefore, it is worth considering the implications of doping CdTe with different impurities.

CdTe is a II-VI semiconductor with a zinc blende lattice formation [17]. However, the wurtzite lattice structure has also been observed [18]. In general, the dopant can replace either Cd (Group II-B) or Te (Group VI-A) in the lattice. Therefore, potential *p*-type dopants are either Group I-B atoms such Cu, Cu and Ag or Group V-A atoms such as N, Sb, As, and P. Similarly,

potential *n*-type dopants are either Group III-A atoms such as Al, Ga, and In or Group VII-A atoms such as Cl, Br, and I.

Acceptor and donor energy levels were calculated by Zhang and Wei at the National Renewable Energy Laboratory using the linearized augmented plane wave method [4]. The results of these theoretical calculations are depicted in Figure 10.



Figure 10: Acceptor and donor transition energy levels in CdTe [4].

First, let us consider the *p*-type doping of CdTe. Of the Cd-substituting dopants, it was found that Na and Ag give the shallowest acceptor levels. Of the Te-substituting dopants, N, P, and As give the shallowest acceptor levels. Note that the intrinsic Cd vacancy (V_{Cd}) also has a relatively shallow acceptor level. Although all of these options have potential to give high hole concentrations, several can be eliminated by considering other factors. For example, it was found that if sodium were used as a *p*-type dopant (N_{aCd}), the lowering of the Fermi energy stabilizes the interstitial Na (Na_i) donor defect [4]. Therefore, self-compensation makes sodium an unsuitable choice for *p*-type doping. Nitrogen was also found to be an unsuitable dopant due to the high energy of formation of the N_{Te} defect [4]. Therefore, P, As, and Ag remain as potential *p*-type dopants. However, the relatively deep acceptor energy of arsenic in comparison to the others suggests that it may give rise to a crystal with poor conductivity. From the right side of Figure 10, one can see shallow donor levels can be formed by substituting Cd with Al, In, or I. Furthermore, Cu and Na interstitials can also act as *n*-type dopants with shallow donor levels. However, the sodium interstitial is not an effective donor due to the self-compensation relationship with Na_{Te} described previously. There is a similar relationship between the Cu interstitial (Cu_i) and the Cu_{Cd} defects, rendering Cu_i an ineffective source of electrons. Another limitation for some *n*-type dopants is the formation of *DX* centers [4]. *DX* centers form as a result of breaking single bonds and are common donor-compensating defects in both II-VI and III-V semiconductors [19]. Further calculations indicated that Al and In are not good *n*-type dopants because the formation energy of these defects is increased due to the formation of *DX* centers [4]. However, *DX* centers were not found to be limiting in the case of iodine doping.

In summary, theoretical calculations indicate that P, As, and Ag may be effective *p*-type dopants and iodine may be an effective *n*-type dopant. There have been numerous successful attempts at doping CdTe with a selection of these substances. CdTe wafers were successfully doped with phosphorous at a concentration on the order of 10^{18} cm⁻³ using a vertical Bridgman setup [20]. However, the effectiveness of this doped CdTe in solar cells was difficult to assess due to the degradation of efficiency after the annealing process [20].

The traveling heater method (THM) was used for the growth of As-doped CdTe, giving dopant concentrations on the order of 10^{15} - 10^{16} cm⁻³ [21]. Interestingly, it was observed that doping with arsenic was limited to below 10^{17} cm⁻³. Furthermore, characterization of these crystals possibly indicated the presence of unknown deep-level defects [21].

Finally, iodine doping of CdTe has been achieved in concentrations up to 10^{18} cm⁻³ using molecular beam epitaxy (MBE) [22]. Using the same method, In-doping was found to be less effective, providing further support for iodine as an *n*-type dopant in CdTe [22].

The literature regarding *n*- and *p*-type doping of CdTe demonstrates a wide variety of techniques that may be used to attain modest dopant concentrations. One could evaluate the effectiveness of these dopants by incorporating the doped crystals into solar cell devices and determining efficiencies. However, a more analytical approach would allow for a determination of exactly how the doping process affects solar cell efficiency, especially through the formation of deep-level defects.

2.5) Electron Paramagnetic Resonance

2.5.1) Physics of EPR

Electron paramagnetic resonance (EPR) is a powerful analytical tool for characterizing material defects. The basis of EPR is that the spin quantum number of an electron, m_s can take a value of either +1/2 or -1/2, referred to as "spin up" or "spin down." The intrinsic angular momentum of an electron gives rise to a magnetic moment, referred to as the Bohr magneton (μ_B). In the absence of a magnetic field, the two spin states are degenerate. Therefore, a population of electrons will be distributed approximately evenly between the two spin states. However, in the presence of a magnetic field, the magnetic moment of an electron will align either parallel (lower energy) or antiparallel (higher energy) to the magnetic field. This energetic splitting is known as the Zeeman effect, and increases linearly with magnetic field strength [5]. The difference between these energies ΔE is given by

$$\Delta E = h\nu = g\mu_B B \tag{10}$$

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where *B* is the magnetic field flux density. For a free electron, *g* has a value of 2.00232 [5]. However, the specific environment of an electron will alter the value of *g*, as will be discussed shortly.

By the Pauli Exclusion Principle, two electrons in the same quantum mechanical system cannot have an identical set of quantum numbers. Therefore, two paired electrons (in a bond, for example) must have opposite spins. The spin of one of these electrons cannot be flipped, as this would result in a pair of electrons with the same spin. However, unpaired electrons can alternate between spin up and spin down. Due to the lower energy of the spin down (spin -1/2) state in a magnetic field, a greater fraction of unpaired electrons will occupy this state. However, these electrons can absorb electromagnetic radiation of energy $hv = \Delta E$ and transition to the higher energy (spin $+\frac{1}{2}$) state. Thus, if electromagnetic radiation is incident on a material with unpaired electrons in the presence of a magnetic field, power will be absorbed by the material when the resonance condition is met [5]. Using the experimentally determined resonance conditions, the value of g can be calculated [5]. This value provides insight into the nature of the site being occupied by the unpaired electron. This allows for the determination of the types of defects that are dominant in a material. Deviations in resonance conditions from those of a free electron are primarily a consequence of two phenomena: spin-orbit coupling and nuclear-hyperfine interactions.

Spin-orbit coupling can be thought of as the effect of the angular momentum of an electron's wave function on that electron's local magnetic field [5]. Although rigorous treatment of this effect requires a firm understanding of quantum mechanics, a qualitative description will suffice. Consider an electron that is localized around a nucleus as described by its wave function.

Assume that this wave function has an angular momentum component (which is always true, except for the case of the 100% *s*-type wave function) [5]. From the reference frame of this electron, the nucleus to which it is bound is orbiting with the same angular momentum. Therefore, the "motion" of this charged nucleus will generate a small magnetic field around the electron. This small magnetic field will shift the value of the external magnetic field at which electron resonance occurs by the same amount. The effects of spin-orbit coupling are expressed in a change in the *g*-factor from 2.00232 to a generic value. The magnitude of this deviation is dependent on the average distance between the electron's orbital angular momentum [5]. Since the magnetic field due to spin-orbit coupling has a specific orientation, the change in resonance conditions will also depend on the orientation of the material's crystal lattice relative to the external magnetic field. Therefore, in general, *g*-factors are expressed as a second rank tensor in order to capture the anisotropy of spin-orbit coupling effects [5].

Unlike spin-orbit coupling, which is the result of the interactions between a coupled electron and nucleus, nuclear-hyperfine interactions are a consequence of magnetic nuclei. As with spin-orbit coupling, these interactions will be described here in a mostly qualitative manner.

Like electrons, some nuclei possess an intrinsic angular momentum, giving rise to a magnetic moment. Nuclei with odd numbers of neutrons and protons will have nuclear magnetic moments [5]. A nuclear magnetic moment will create a magnetic field that affects the local magnetic field of an electron. A spin $\frac{1}{2}$ nucleus (e.g. phosphorous) can have a spin of $+\frac{1}{2}$ or $-\frac{1}{2}$, and thus can shift the resonant magnetic field of an electron either upfield or downfield. This results in the resonant condition for an electron being split into two distinct sets of resonant conditions. Nuclei can also have spins other than $\frac{1}{2}$. For example, nitrogen, with a spin of 1 (m_s

= -1, 0, or +1) can shift the resonant field of an electron upfield, downfield, or not at all. This results in three different sets of resonance conditions for the electron. The degree of this splitting is dependent on the orbital type of the electron. By examining the anisotropy of splitting patterns, the ratios of p and s orbital character can be determined, providing valuable information about the defect site. The effects of nuclear-hyperfine interactions are typically represented by the addition of a "hyperfine tensor" to the resonance conditions of an electron.

In summary, conditions under which an electron will absorb energy and flip spins are dependent on the properties of the nucleus to which which the electron is localized, as well as the presence of magnetic nuclei. Therefore, if one is able to experimentally determine the exact resonance conditions, it is possible to characterize the environment of the resonating electrons within a crystal lattice. Since unpaired electrons typically reside at crystal defects (e.g. vacancies, substitutions, dangling bonds, etc.), EPR allows for determination of the specific defects that are present in a material [5]. This information is extremely useful in assessing how a material will limit the performance of a device into which it is incorporated.

2.5.2) Practical Aspects of EPR

Determination of the resonance conditions for an unpaired electron includes finding a specific combination of magnetic field strength and electromagnetic wave frequency for which power is absorbed by the electrons. In practice, an EPR experiment consists of keeping a fixed electromagnetic wave frequency while varying the magnetic field. The electromagnetic radiation is typically in the X-band of the microwave region, around 9-10 GHz. Magnetic fields are typically on the order of thousands of Gauss (1 Gauss = 0.1 mT). A sample under analysis will be placed in a microwave cavity that is optimally sized for setting up standing microwaves. The

amount of microwave power that is reflected from the cavity is measured in the microwave bridge as well. When a standing wave is set up in the microwave cavity, the reflected power will be at a minimum, indicating that the cavity has been tuned.

Microwaves are generated in a microwave bridge and transmitted into the microwave cavity. The microwave cavity is positioned in the center of a large magnet that is capable of creating a spatially uniform magnetic in the area of the sample. With the microwave frequency fixed, the current through the coils in the magnet will be increased, resulting in an increase the magnetic field in the area of the sample. The magnetic field is then swept through a specified range. When the resonance conditions are met, the amount of power being reflected from the cavity will decrease, as shown in Figure 11.



Figure 11: Reflected microwave power at the resonant frequency vres [23]

Unfortunately, the amount of noise present in a spectrum such as this will typically make identification of the signal of interest very difficult or impossible. This makes a simple experiment like the one described somewhat impractical. However, there are several important parameters and features of EPR experiments that, when optimized, will improve the signal-tonoise ratio of a spectrum.

2.5.2.1 Field Modulation

One feature of EPR experiments that serves to improve the signal-to-noise ratio of a spectrum is field modulation. The main coils of the EPR magnet generate a magnetic field that increases linearly with time over the specified range. However, an additional, smaller set of coils generates an oscillating magnetic field. Typically, this so-called modulation field has a frequency of around 100 kHz and an amplitude between one and fifteen Gauss. Figure 12 depicts the net field that results after modulation is added [5]. With this modulated field, an EPR response will oscillate with the same frequency and phase as the modulation field. This signal is passed through a frequency-sensitive and phase-sensitive lock-in amplifier. As a result, the signal of interest will be amplified, while noise of other frequencies will not, giving in a cleaner spectrum.



Figure 12: EPR magnetic field variance after adding modulation [5]

With field modulation, what is actually being recorded is the change in signal intensity over each period of the modulation. One important consequence of this is that EPR signals are generally plotted as a first derivative of the true signal, as demonstrated in Figure 13. Viewing a derivative of an EPR signal can be advantageous, as it causes subtle features of a signal's shape to be emphasized.



Figure 13: Effect of field modulation on signal shape [23]

Although modulation is essential for improving the signal-to-noise ratio, one must be cautious in selecting the modulation amplitude. While a larger modulation amplitude will initially improve signal amplitude, too high of an amplitude will actually have a negative impact on the signal-to-noise ratio. If the amplitude of the modulation exceeds the width of an EPR signal, that signal will start to broaden and decrease in amplitude, eventually disappearing entirely. For these reasons, the lock-in amplifier yields the strongest response when the lock-in modulation amplitude is smaller than the narrowest feature of interest.

2.5.2.2 RC Filter Time Constant

In addition to field modulation, the incorporation of a low pass RC filter with time constant τ can reduce the amount of noise present in EPR spectra. Noise with frequencies greater than $1/\tau$ will be filtered out. In order to prevent reduction in signal amplitude, the time constant should be chosen such that it takes at least five time constants to pass through the EPR signal during data collection [5]. For example, with a time constant of one second and a five Gauss wide signal, the magnetic field should be swept through at a rate of one Gauss per second. The total sweep time can be chosen accordingly.

2.5.2.3 Microwave Power

At very low microwave powers, few of the unpaired spins in a material will be flipped [5]. As microwave power increases, more spins will be flipped. This results in a greater signal amplitude. Signal amplitude increases linearly with the square root of microwave power [24]. However, once a certain power is reached, the spin system will be "saturated," meaning that spins are being flipped to the higher energy state at the same rate they are returning to the lower energy state. This will lead to a net decrease in power absorption, and thus a decrease in signal intensity. A particular example of this relationship between signal intensity and microwave power is shown in Figure 14.



Figure 14: Saturation of an EPR signal as microwave power increases [24]

In order to maximize the signal-to-noise ratio, one must run a series of EPR scans at varying power levels. By observing the relationship between the measured signal intensities and microwave power, one can select a power for which the signal intensity is high, but has not yet begun to saturate.

2.5.2.4) Temperature Effects

It is worth noting that EPR measurements can be highly sensitive to temperature. This is due to the fact that, by Equations 4 and 5, the concentration of charge carriers in a semiconductor is exponentially dependent on temperature, with high temperatures giving higher concentrations. At higher temperatures, electrons/holes will have sufficient thermal energy to ionize from their donor/accepter cores. Similarly, shallow defects may not effectively trap charge carriers at high temperatures. Conduction electrons and holes do not give rise to strong EPR signals – rather, they produce broad, often unnoticed peaks. At low temperatures, however, electrons and holes will return to their respective donors and acceptors, or be trapped in defects. For this reason, liquid nitrogen and liquid helium are sometimes used to decrease the temperature of samples for EPR. In addition, the decrease in conductivity of a sample at low temperatures will facilitate the tuning process.

2.6) EPR with CdTe

Numerous EPR studies have been conducted with the goal of characterizing deep level defects in CdTe. Some of these studies have been specifically directed towards identifying defects related to manufacturing or processing techniques. One such technique is the previously discussed CdCl₂ treatment [1]. In one study at Penn State University, samples that had been treated with CdCl₂ and Cu were analyzed by EPR [25]. The results of this study suggested interactions between CdCl₂ and Cu. Furthermore, it was believed that Cu affected the concentrations of intrinsic defects, most likely the Cd vacancy [25]. However, it was difficult to observe subtle effects of these processing treatments due to the strong presence of manganese impurities. The 5/2 spin of manganese results in a six-peak EPR signal. The presence of manganese in CdTe has been observed in other EPR studies as well [26].

A separate EPR study specifically attempted to characterize the effects of metal impurities in CdTe [27]. As was discussed in Section 2.4.2, transition metal impurities can act as

important deep-level defects. This study included the identification of nickel, cobalt, iron, and chromium in CdTe. Iron is of particular importance since it is a common residual impurity in CdTe [27].

A large number of the EPR studies involving CdTe have been directed towards characterizing intrinsic defects in CdTe crystals [27], [28]. The defects of greatest interest have been the Cd and Te vacancies (V_{Cd} and V_{Te}). The V_{Te} defect has an energy level close to the center of the CdTe bandgap [4]. Therefore, if a particular dopant were to cause an increase in V_{Te} concentration, the efficiency of a solar cell could be severely decreased. For V_{Cd} , a *g* value of approximately 1.95 to 2.15 (depending on orientation) has been reported [29]. For V_{Te} , an isotropic *g* value of 2.00 has been reported [30].

Finally, a select number of CdTe EPR studies have examined the effects of intentional *n*or *p*-type doping. For instance, CdTe crystals heavily doped with chromium were found to give rise to two clear EPR signals which were specific to chromium doping [31]. Another study identified an isotropic EPR signal at g = 1.65 which was observed in Al-, In- and Cl-doped CdTe [32]. Finally, EPR has been used to explore the role of oxygen in CdTe crystals [18]. Although oxygen does not act as a donor or acceptor, it has been found to improve the characteristics of *p*type CdTe [33]. In this study, varying heat treatments were used to introduce varying amounts of oxygen to the crystals, in the form of TeO₂. It was found that for higher amounts of oxygen, an EPR signal at g = 2.0002 was observed [18].

Although these studies do not explore the effects of the dopants being examined in this experiment, they are still highly relevant. The compiled EPR data serves as useful reference material for attributing any observed EPR signals to particular defects, without requiring quantitative analysis. If an experimentally obtained EPR spectrum has a signal that matches the

description of a previously observed signal, we may be able to exclude the possibility that the corresponding defect is formed as a result of the dopants. The results of these studies may allow us to determine whether the introduction of specific dopants affects the concentrations of intrinsic defects.

Finally, since the samples under analysis include As-, P-, and I- doped CdTe, interpretation of EPR spectra may require knowledge of nuclear spins for these dopant atoms. This information is summarized below in Table 1:

Nucleus	Abundance	Spin
³¹ P	100%	1/2
⁷⁵ As	100%	3/2
¹²⁷ I	100%	5/2
¹¹¹ Cd	12.75%	1/2
¹¹³ Cd	12.26%	1/2
¹²³ Te	0.9%	1/2
¹²⁵ Te	7.0%	1/2

Table 1: Spins of relevant nuclei[34]

Chapter 3

Experimental

3.1) Samples used in this experiment

The samples used in this experiment were a collection of doped and undoped CdTe

crystals and powders. The details of these samples are summarized below in Table 1:

Sample	Description	Mass (g)
Undoped CdTe	Powder	0.175
As-doped CdTe	Powder	0.191
I-doped CdTe	Powder	0.190
P-doped CdTe	Powder	0.190
As-doped CdTe	Single crystal	0.015
I-doped CdTe	Single crystal	0.007
P-doped CdTe	Single crystal	0.198

Table 2: Summary of samples under analysis

All samples were grown by the transfer-heater method. Measurements were made directly on the samples, so no special preparation was required other than transferring powders to test tubes.

3.2) Experimental Details

The components of the spectrometer setup are depicted below in Figure 15.



Figure 15: EPR experimental setup

This experiment utilized an X-Band Bruker Biospin EPR spectrometer (6). The major components of the spectrometer are the EPR magnet (1), microwave cavity (2), microwave bridge (3), frequency counter (4), power supply (5), and heat exchanger (7). The only other equipment used was a liquid nitrogen dewar (visible in the microwave cavity in Figure 15) in which the crystal samples were held while collecting data, both with and without liquid nitrogen.

3.3) Procedures

With the spectrometer in standby mode (60 dB attenuation of microwaves), the sample was inserted into the microwave cavity, ensuring that the sample itself was located at the center of the cavity. The spectrometer was then switched into tuning mode (25 dB attenuation). After

locating the frequency at which the cavity was in resonance, the spectrometer was turned to operate mode and the attenuation was decreased in 1 dB increments until the desired power was reached. While decreasing the power, adjustments were made to the signal phase, bias, and frequency settings to ensure that the cavity remained in tune. The iris screw was also raised or lowered appropriately in order to achieve critical coupling while fine-tuning the cavity. With the desired power reached and the cavity in tune, the spectrometer was then ready to collect EPR data. The appropriate settings were then selected for the particular scan: center magnetic field (CF), magnetic field sweep width (SW), modulation amplitude (MA), time constant (TC), sweep time (ST), and the number of scans to be averaged. For all experiments, the modulation frequency was 100 kHz. The scan was then initiated.

For the single crystal samples, some measurements were made around liquid nitrogen temperature. In these cases, the nitrogen dewar was cleaned with ethanol and air-dried when samples were exchanged. Simply pouring liquid nitrogen into the dewar resulted in tuning difficulties due to the vigorous boiling of the nitrogen. Rather, a swab of cotton was placed above the sample at the neck of the dewar and nitrogen was poured into the wide portion of the dewar, suspended above the sample by the cotton. Therefore, the samples under analysis were likely not brought entirely down to liquid nitrogen temperature (77 K). For long scans, more liquid nitrogen had to be added to the dewar after approximately 35 minutes. No artifacts were observed as a result of adding nitrogen mid-scan. However, out of caution, nitrogen was only added while the magnetic field was outside of the region of interest.

When testing on a particular sample was complete, the sample was removed and the dewar was allowed to dry overnight outside of the cavity. The dewar was suspended with the

open end facing downwards in order to prevent any condensation or ice on the outside of the tube from dripping inside.

Chapter 4

Results and Discussion

4.1) Preliminary Data

Prior to collecting data on the CdTe samples, an EPR spectrum was obtained for the empty microwave cavity in order to identify any background signals from the cavity itself (Figure 16). Similarly, spectra were obtained for the empty dewar at both room temperature (Figure 17) and with liquid nitrogen (Figure 18).



Figure 16: Empty microwave cavity (RT)



Figure 17: Empty Dewar (RT)



Figure 18: Empty Dewar (LN)

As one can see, there was a moderate amount of background signal even without a sample present. Unfortunately, some of this background could be mistaken for a true signal and

occurs in the regions where signals might be expected. This background must be taken into account when interpreting future spectra.

4.2) Powder Samples

First, spectra were collected for the four powder samples at room temperature. The following spectra were collected using a time constant of 0.327s, a modulation amplitude of 4 G, and a microwave power of 10 mW.



Figure 19: Undoped CdTe powder wide spectrum



Figure 20: As-doped CdTe powder wide spectrum



Figure 21: P-doped CdTe powder wide spectrum



Figure 22: I-doped CdTe powder

In all four spectra, there is a significant "signal" at around 3100 Gauss. However, this feature appears to correspond to the large background signal seen in Figure 16 at the same magnetic field. In the case of the P-doped sample, it appears that this background signal occurs in the middle of a very wide (~1000 G) signal. Unfortunately, this overlapping background makes quantitative analysis of this signal rather difficult. The As-doped sample gave rise to a large signal with g = 2.0026, in a region free of significant background. The following spectrum was obtained for the same signal with a narrower sweep width.



Figure 23: As-doped CdTe powder, narrow spectrum.

Let it be noted here that signal "averaging" with this particular software consists of simply adding consecutive spectra together. Therefore, the observed intensities reflect both the actual EPR intensity as well as the total number of scans collected. This explains the discrepancy in signal amplitude between the wide and narrow spectra in Figures Figure 20 and Figure 23. In all cases where relative signal amplitudes were of great quantitative importance, spectra were obtained with identical settings, including the number of added scans.

In order to verify that the spin system giving rise to this signal was not beginning to saturate at the microwave power of 10 mW, spectra were obtained for the same signal at varying powers. The results are depicted in Figure 24 and Figure 25.



Figure 24: EPR spectra for the g = 2.0026 signal in As-doped CdTe, collected at 2, 5, 10, and 20 mW.



Figure 25: EPR signal amplitude of As-doped CdTe powder plotted at several microwave powers

The linear relationship between the EPR signal amplitude and the square root of the microwave power indicates that the signal had not begun to saturate at 10 mW. Therefore, this microwave power was an appropriate choice, and further spectra were collected at this power as well.

In order to quantify the number of spins giving rise to the signal in Figure 23, it was necessary to compare the signal to the signal of a weak pitch standard. This standard is known to have 2×10^{13} spins associated with the strong signal near the free electron *g*.

In general, since an EPR spectrum is essentially the first derivative of the true absorption signal, taking two successive integrals of an EPR signal will yield the area under the true absorption signal. This value is proportional to the number of spins giving rise to the signal. Therefore, the ratio of the second integrals of the unknown signal and the weak pitch signal will give the ratio of the numbers of spins producing each signal. This ratio can be multiplied by the known 2×10^{13} to give the number of spins in the sample. The EPR spectra for the As-doped CdTe and the weak pitch standard, along with their integrals, are shown in Figure 26 and Figure 27, respectively.







Figure 27: Integration of weak pitch signal

From this data, the number of spins in the As-doped CdTe powder can be calculated:

$$\left(\frac{1.431 \times 10^7}{2.135 \times 10^6}\right) \times (2 \times 10^{13}) = 1.34 \times 10^{14} \text{ spins}$$

Using the mass of the sample and the density of CdTe (5.85 g/cm³), the approximate defect concentration was found to be 4.11×10^{15} cm⁻³.

4.3) Room temperature measurements

Preliminary wide scans of the three single crystal samples at room temperature yielded the following spectra:



Figure 28: As-doped CdTe (RT) 7000 G spectrum



Figure 29: I-doped CdTe (RT) 7000 G spectrum



Figure 30: P-doped CdTe (RT) 7000 G spectrum

The three doped samples all presented the same broad, high-intensity signal centered around 3000 G (Figure 28, Figure 29, and Figure 30).

4.4) Liquid nitrogen measurements

Following room temperature measurements, similar measurements were made at liquid nitrogen temperature in order to observe any appearance or disappearance of signals. A preliminary wide scan of the As-doped CdTe sample did not show any observable signals. However, a narrowed scan revealed a signal at ~3350 G (Figure 31). The spectrum in Figure 32 shows this signal in more detail.



Figure 31: As-doped CdTe (LN) 1000 G spectrum



Figure 32: As-doped CdTe (LN) 100G spectrum

The spectrum in Figure 32 was replicated using a modulation amplitude of only three Gauss, which was not observed to narrow the signal. Therefore, it was concluded that five Gauss modulation was appropriate for examining this signal. Furthermore, in order to verify that this signal was not saturated at the microwave power used, the signal amplitude was measured at a variety of microwave powers. The results of these measurements are show in Figure 33.



Figure 33: Signal amplitude vs. microwave power for signal at 3350G

Although Figure 33 does not perfectly demonstrate the expected linear relationship between signal amplitude and the square root of microwave power, it does not appear that the spin system causing this signal was being saturated at the power being used.

Moving on, similar spectra were obtained for the I-doped CdTe sample: A preliminary wide scan did not display any signals (Figure 34). However, given the position of the signal in the As-doped CdTe sample, an additional spectrum was collected in the region around 3350 G (Figure 35).



Figure 34: I-doped CdTe (LN) 1500 G spectrum



Figure 35: I-doped CdTe (LN) 150 G spectrum

Clearly, the I-doped CdTe exhibits a very similar signal to that of the As-doped CdTe sample, albeit lower in amplitude. However, the difference in signal amplitude is not surprising given that the I-doped CdTe sample was much lower in mass.

Next, these scans were repeated for the P-doped CdTe sample. However, neither wide nor narrow spectra yielded meaningful signals (Figure 36 and Figure 37, respectively).



Figure 36: P-doped CdTe (LN) 1500 G spectrum



Figure 37: P-doped CdTe (LN) 500 G spectrum

It was found that, despite the large size of the P-doped CdTe crystal, the microwave cavity was tuned with much greater ease than with the other samples. Adjusting microwave power to over 100 mW did not give rise to any signals.

4.5) Return to Room Temperature

Interestingly, none of the spectra obtained at liquid nitrogen temperature displayed the broad signal that dominated the room temperature spectra for the single crystal samples. Therefore, attempts were made to reproduce this broad signal at room temperature. The resulting spectra for the As-doped CdTe, I-doped CdTe, and P-doped CdTe did not display the previously seen signal. Manipulation of EPR parameters did not lead to a reappearance of the signal.

Chapter 5

Conclusions

The most significant result of this experiment was a strong EPR signal in As-doped CdTe powder. The absence of this signal in the other three powders indicates that this signal is a direct result of doping with arsenic. Therefore, it can reasonably be inferred that arsenic doping leads to the formation of a compensating defect that could potentially act as a deep-level recombination center. Given the relatively deep energy level of arsenic acceptors, it is possible that arsenic does not ionize as effectively as iodine and phosphorous. However, it is unlikely that un-ionized holes are the source of this signal, since the ¹/₂ nuclear moment of arsenic would give rise to hyperfine splitting in an associated signal. Therefore, it is likely that this signal is associated with an intrinsic defect in CdTe. The symmetry of the powder signal suggests that this defect is isotropic. Therefore, it is unlikely that this signal is caused by a cadmium vacancy, which is characteristically anisotropic. However, g values of around 2.000 have been reported for the tellurium vacancy in CdTe (V_{Te}) [35]. Given the similarity of this value to the experimentally observed g = 2.0026, it is reasonable to hypothesize that the tellurium vacancy was the source of the observed signal. Comparison of this signal to a weak pitch standard determined the density of this defect to be 4.11 cm⁻³, although automatic scaling by the EPR software may have compromised the accuracy of this result.

Additionally, a broad signal was observed for the P-doped powder. Unfortunately, the background signal of the microwave cavity severely limited analysis of this signal. This signal,

as well as the spectra of all samples in this study, will be explored in more detail following replacement of the microwave cavity.

Data collected for the three single crystal samples at room temperature were largely inconclusive. Initially, the three doped samples gave rise to a consistent, large signal with *g* values in the range of 2.1-2.4. However, spectra collected for these samples at room temperature post-liquid nitrogen did not display this signal. It is unlikely that the initial signals were due to impurities, since care was taken to clean the dewar when samples were exchanged. Furthermore, no other materials that were analyzed in this spectrometer in the recent past displayed this signal. Therefore, the nature of this signal remains a mystery. It is worth exploring whether the nature of particular defects in the CdTe may have changed upon exposure to liquid nitrogen.

Spectra collected at liquid nitrogen temperatures yielded reproducible signals for the iodine (g = 2.0003) and arsenic-doped (g = 2.0002) samples. A similar signal was not observed for the phosphorous-doped sample. Given the similarity in g values to the arsenic-doped powder, it is likely that these signals were caused by the same defect. The amplitude of this signal in the iodine-doped single crystal sample was lower than for the arsenic-doped single crystal. Furthermore, this signal was not observed in the iodine-doped powder. Therefore, it appears that the responsible defect (perhaps V_{Te}) is formed in a lower concentration as a result of iodine doping than for arsenic doping.

If the tellurium vacancy were in fact the defect responsible for the observed signals, the results of this experiment would suggest that arsenic doping in CdTe is not ideal due to the formation of this compensating defect in moderate concentration. The tellurium vacancy has an energy level of 0.71eV below the bottom of the conduction band, very close to the center of the

CdTe band gap. Therefore, the tellurium vacancy could act as a deep-level recombination center, ultimately limiting solar cell performance. Additionally, the more subtle presence of this signal in iodine-doped CdTe suggests that iodine may not be an ideal *n*-type dopant for CdTe. In contrast, since this signal was not observed in either of the phosphorus-doped samples, phosphorus should still be considered as a *p*-type dopant in CdTe for solar cell applications. Further studies should explore the physical relationship between the addition of these three specific dopants and the tellurium vacancy in order to assess the validity of this hypothesis.

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ACADEMIC VITA

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EDUCATION

Bachelor of Science in Engineering Science, May 2018 **Schreyer Honors College**

The Pennsylvania State University, University Park, PA

• Honors Thesis: Detection of Efficiency-Limiting Defects in Cadmium Telluride

RESEARCH

Undergraduate Thesis Student, Engineering Science & Mechanics Department

Semiconductor Spectroscopy Laboratory, University Park, PA

- Operated hardware & software for electron magnetic resonance experiments
- Collaborated with graduate staff to develop new hardware for EPR and EDMR
- Innovated experimental setups for detecting defects in CdTe and Ga₂O₃ crystals

WORK EXPERIENCE

Teaching Assistant, Biology Department

Eberly College of Science, University Park, PA

- Responsible for independently leading a physiology lab section of 18 students
- Oversaw lab activities and enforced safe and ethical laboratory techniques •

Student Intern

Summit Health, Chambersburg, PA

- Shadowed doctors across a wide variety of health care fields •
- Interacted with hospital patients and assisted with daily tasks ٠

VOLUNTEER EXPERIENCE

Medical Assistant

Saint Francis Hospital, Mutolere, Uganda

• Assisted neonatal ICU nursing staff with newborn care and surgical procedures

HONORS & AWARDS

- Dean's List: All semesters
- President's Freshman Award, 2015
- President Sparks Award, 2016
- Evan Pugh Senior Scholar Award, 2017

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