

DOPING STUDIES OF CADMIUM TELLURIDE, CADMIUM MAGNESIUM
TELLURIDE, AND CdTe/CdMgTe DOUBLE HETEROSTRUCTURES
GROWN USING MOLECULAR BEAM EPITAXY

by

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ABSTRACT

CdTe is one of the leading materials used in thin-film photovoltaic (PV) devices due to some of its basic properties such as its ability to permit both *n*- and *p*-type doping, its relatively high absorption coefficient for photons in the visible range, and its direct band gap of 1.514 eV at room temperature, which is near the optimal band gap for solar energy conversion. Despite the near optimal band gap, the highest power conversion efficiency in a CdTe solar cell to date, achieved using polycrystalline CdTe, stands at 21%. This is far less than the Shockley–Queisser limit, which is about 32% for a single-junction cell under AM 1.5 illumination condition. Research efforts have shown that short circuit current (J_{sc}) is near its theoretical limit, implying that strategies to improve cell efficiency will have to be contingent on improving open-circuit voltage (V_{oc}) and fill factor. Heavy doping has the potential to improve V_{oc} . There is also evidence that inclusion of a $\text{Cd}_{1-x}\text{Mg}_x\text{Te}$ barrier in a solar cell structure may improve open circuit voltage, and, ultimately, cell efficiency.

Doped and undoped CdTe layers were grown by molecular beam epitaxy (MBE). Secondary ion mass spectrometry (SIMS) characterization was used to measure dopant concentration, while Hall measurement and the capacitance-voltage technique were used for determining carrier concentration. Photoluminescence intensity (PL-I) and time-resolved photoluminescence (TRPL) techniques were used for optical characterization.

The incorporation and limits of iodine and arsenic dopants in CdTe were studied. Maximum *n*-type carrier concentrations of $7.4 \times 10^{18} \text{ cm}^{-3}$ for iodine-doped CdTe and $3 \times 10^{17} \text{ cm}^{-3}$ for iodine-doped $\text{Cd}_{0.65}\text{Mg}_{0.35}\text{Te}$ were achieved. Studies suggest that electrically active doping with iodine is limited with dopant concentration much above these values. Dopant activation of about 80% was observed in most of the iodine-doped CdTe samples. The estimated activation energy is about 6 meV for CdTe and the value for $\text{Cd}_{0.65}\text{Mg}_{0.35}\text{Te}$ is about 58 meV. Iodine-doped CdTe samples exhibit long lifetimes with no evidence of photoluminescence degradation with doping as high as $2 \times 10^{18} \text{ cm}^{-3}$ while indium shows substantial non-radiative recombination at carrier concentrations above $5 \times 10^{16} \text{ cm}^{-3}$. Also, maximum *p*-type carrier concentration of $2 \times 10^{16} \text{ cm}^{-3}$ for arsenic-doped CdTe was achieved. Dopant activation greater than 20% was observed in most of the arsenic-doped CdTe samples. The process compatibility of iodine and magnesium in CdTe was evaluated for the solar cell device. Iodine was shown to be thermally stable in CdTe at temperatures up to 600 °C and magnesium showed a slow diffusion at 500 °C. Doped CdTe structures were used to make solar cell device structures, where open circuit voltage up to 880 mV and fill factor up to ~60% were measured.

1. INTRODUCTION

Doping studies of cadmium telluride (CdTe), cadmium magnesium telluride (CdMgTe), and CdTe/CdMgTe double heterostructures grown using molecular beam epitaxy is a venture that is part of a bigger project, entitled “Approaching the Shockley-Queisser limit with epitaxial CdTe.” This project was awarded to the National Renewable Energy Laboratory (NREL) by the U.S. Department of Energy (DOE) under the Foundational Program to Advance Cell Efficiency (FPACE). This FPACE project involves partnership from NREL, First Solar, Colorado State University, the Colorado School of Mines, Washington State University, and Texas State University. Texas State University was tasked with the molecular beam epitaxy (MBE) growth of CdTe-based structures and their material characterization. The goal of this FPACE project is to use MBE-grown epitaxial CdTe structures to explore the fundamental limits of doping, surface passivation, carrier lifetime, and carrier mobility in CdTe in order to increase CdTe solar cell efficiency from 18.7% to 24% in three years. This project is part of the ongoing effort by DOE towards making alternative energy affordable and secure as concerns grow about the depletion and environmental impact of retrieving non-renewable energy. The photovoltaic solar cell technology, which converts sunlight into electricity, is one of the major technologies for achieving alternative energy.

Figure 1 illustrates the structure and energy conversion process of a photovoltaic device. The device is composed of a junction between an n-type and p-type semiconductor and electrodes. Photons absorbed by the solar cell excite electrons from the valence to the conduction band where the applied electric field separates them. Separation of negative electrons and positive holes at the p-n junction creates a voltage difference and allows the

current to flow through a connected load.¹

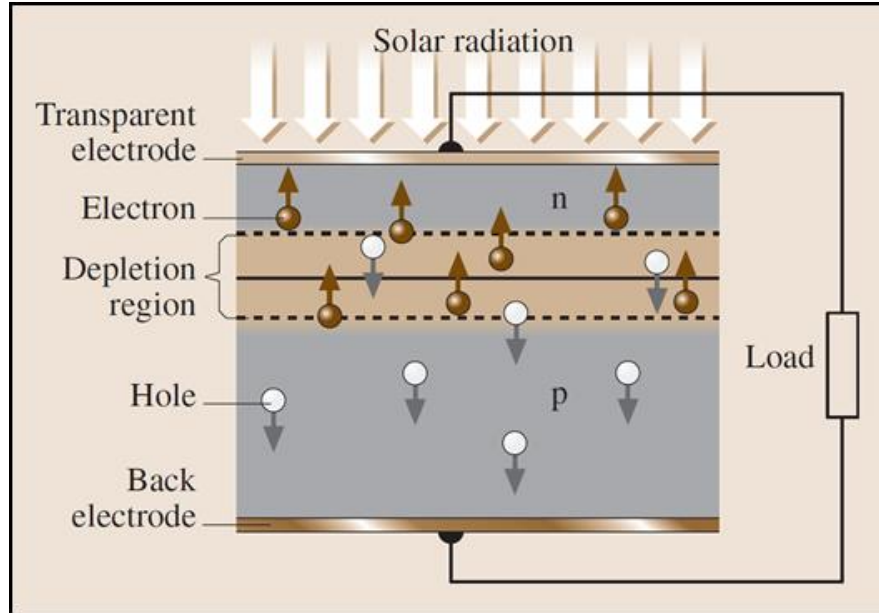


Figure 1. Energy conversion process in a photovoltaic device.¹

Although photovoltaics have been made using many semiconductors, CdTe—a II-VI compound semiconductor—provides many advantages for this application. Some of the considerations in choosing photovoltaic materials are: the band gap of the absorbing material, diffusion length of minority carriers, junction properties, and stability for long term operation.² CdTe is an excellent material for solar cell application due to its high optical absorption coefficient for photons and its direct band gap, which is close to ideal for single-layer solar cell conversion efficiency^{1, 3} as shown in Figure 2.

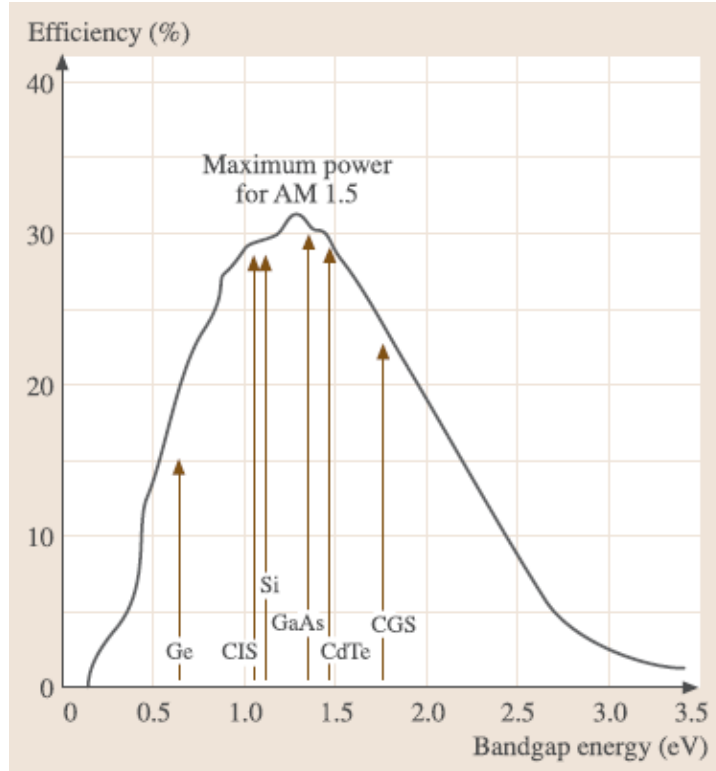


Figure 2. Plot of ideal efficiency against band-gap energy for a single-junction cell for AM 1.5 illumination.

1.1 II-VI photovoltaic systems

The early stage of II-VI thin-film photovoltaics was dominated by copper sulfide (CuS), a semiconductor with a band gap of 1.55 eV that serves as a p-type material, and cadmium sulfide (CdS), a direct band gap semiconductor with a band gap of 2.42 eV that serves as an n-type material. The diffusion of Cu into CdS can cause CuS to have different phases at room temperature allowing it to exhibit different photovoltaic properties and change from one phase to another during cell operation, which gives rise to complexity in the CuS/CdS photovoltaic system.²

The effects of Cu diffusion in CuS/CdS systems resulting in degradation issues necessitated the search for an alternative material that could be used as a p-type material to form an adequate heterojunction with CdS. CdTe became a candidate to replace CuS

because polycrystalline thin-film deposition can be achieved in ways similar to those of CdS. Also, CdTe can be made into either p-type or n-type materials.²

Thin-film heterojunctions continue to be attractive because of their ease of fabrication and potential for low-cost devices. The CdS/CdTe heterojunction device remains attractive to the photovoltaic industry because of its band gap alignment and cost-effective production, but there are still drawbacks to its use: Kirkendall void formation caused by sulphur out-diffusion,⁴ CdS optical absorption losses, impurity diffusion and grain-boundary effects, interdiffusion between CdTe and CdS, and large-lattice mismatch between CdTe and CdS.⁵ Studies have shown that S out-diffusion can lead to significant degradation in the performance of the CdS/CdTe heterojunction device.⁴

The degradation problem associated with the CdS/CdTe heterojunction has led to the search for an alternative junction that is chemically stable. One such alternative is the CdTe/CdMgTe heterostructure, which is actively studied for its ability to overcome some of the challenges associated with the CdS/CdTe heterostructure. The wide band-gap CdMgTe barrier confines photocarriers and prevents rapid recombination at the CdTe surface. The heterostructure formed by CdTe and CdMgTe possesses a type-I band edge alignment.

In addition, the power conversion efficiency CdTe solar cell has been reported to be limited by grain boundaries in polycrystalline CdTe, low dopability, low minority carrier lifetime, energy barriers at contacts, and compensation from impurities.⁶⁻⁹ One of the major strategies for improving solar cell efficiency is ensuring high open-circuit voltage. Open-circuit voltage depends on excess carrier density,¹⁰ hence improving the dopability of CdTe will positively impact the efficiency of CdTe solar cells. In addition, another

strategy for improving efficiency is ensuring high minority-carrier lifetime. The big-picture purpose of this research endeavor is to improve the efficiency of CdTe solar cells by carefully choosing dopants and obtaining a deep understanding of the related doping mechanism.

1.2 Basic CdTe Properties

CdTe possesses electrical and optical properties that are useful for solar energy absorption and conversion. CdTe is a compound semiconductor consisting of Cd, a group IIB element that is also a transition metal, and Te, a group VIA element that is a semimetal. The atomic number of Cd is 48 while that of Te is 52. Both elements are located on row four of the periodic table. The average atomic number of CdTe is 50. CdTe, when compared with other IIB-VIA compounds, has a low melting temperature and a large lattice parameter. Some of the important properties of CdTe are displayed in Table 1.

CdTe has a direct band gap of 1.514 eV at room temperature,¹¹ and a high absorption coefficient for photons.¹² CdTe's direct optimum band gap and high absorption coefficient allow photons with energy greater than its band gap to be absorbed within a few micrometers of CdTe's absorber layer, so less material is needed for the absorber layer design, leading to cost-effective savings.

In addition to its material cost savings and high efficiency, this compound semiconductor permits both *n*- and *p*-type doping, but it has been challenging to achieve doped CdTe with high carrier concentration. The difficulty of doping in II-VI compound semiconductors is due to the semiconductors' self-compensation behavior.¹³

Table 1. Properties of zinc blende CdTe.¹

Property description	Properties of CdTe
Stable phase(s) at 300K	Zinc Blende (ZB)
Melting point (K)	1370
Energy gap E_g at 300 K (eV)	1.514
$dE_g/dT(\times 10^{-4} \text{ eV/K})$	5.4
Bond length (um)	2.806
Lattice constant (a_0) at 300K (nm)	0.6481
ZB nearest-neighbor dist. at 300K (nm)	0.281
ZB density at 300K (g/cm ³)	5.86
Electron affinity χ (eV)	4.28
Specific heat capacity (J/gK)	0.21
Thermal conductivity ($\text{W cm}^{-1}\text{K}^{-1}$)	0.01
Thermal linear expansion coefficient (10^{-6} K^{-1})	5.1
Electron effective mass (m^*/m_0)	0.11
Hole effective mass (m_{dos}^*/m_0)	0.35
Electron Hall mobility (300) K for n = lowish (cm ² /Vs)	1050
Hole Hall mobility at 300K for p = lowish (cm ² /Vs)	100
Exciton binding energy (meV)	12
Average phonon energy (meV)	5.8
Molecular weight (amu)	240.01
Dielectric constant	$\epsilon_0 = 2.27$
Refractive index (ZB)	2.72

Increasing and controlling the conductivity of any semiconductor material remains a key issue for achieving desirable electrical properties. In photovoltaic cells' design, having good electrical transport properties is useful to achieving reasonable efficiency, which means that overcoming the issue of doping in CdTe materials becomes important in harnessing the potential of this material for photovoltaic application.

1.3 Challenges of Doping in CdTe

Although CdTe is an amphoteric II-VI semiconductor that allows both n - and p -type doping, producing CdTe with the sufficient values of minority carriers needed for

photovoltaic application has been challenging, especially for p-type doping. It is easier to achieve n-type doping of CdTe. Other II-VI materials are easily doped with either *n*- or *p*-types but typically not both.¹⁴⁻¹⁶

Potential candidates for doping CdTe are primarily from elements in groups I, III, V, and VII of the periodic table. Group III and group VII are generally considered to be *n*-type dopants in CdTe. Segregation of group VII elements in CdTe is generally low, which helps with doping during crystal growth. Also, this group's low diffusion coefficient ensures stability, and their energy level makes them act as shallow donors in CdTe.¹⁷ While group I and group V are generally considered as p-type dopants in CdTe, the diffusivity of group I elements limit their use as dopants in II-VI compounds.^{18, 19} Group V elements have a lower diffusivity, which makes them attractive as dopants in CdTe.

Candidates that have been successfully used for n-type doping in CdTe are indium (In), chlorine (Cl), bromine (Br), and iodine (I). Indium has become the standard for n-type doping in CdTe MBE growth.²⁰ Indium has been extensively researched and has been used previously in CdTe devices with high V_{oc} . Also, iodine is a promising alternative for n-type doping. Studies show electron concentration as high as almost $1 \times 10^{19} \text{ cm}^{-3}$ can be obtained using I.²¹

The most popular candidates for p-type doping in CdTe are currently arsenic (As), copper (Cu), phosphorus (P), and nitrogen (N). Arsenic seems to be the preferred candidate for *p*-type doping in CdTe due to its thermal stability in CdTe, but it is challenging to achieve high carrier concentration with arsenic doping in CdTe.

1.4 N-type doping in CdTe

Indium is typically the *n*-type dopant of choice and appears to be viable for low doping concentrations. CdTe-based solar cells, however, typically rely on the *n*-side to be heavily doped at levels that have been shown to be problematic for doping with In.²² In addition, In is not an effective dopant in materials like CdMgTe, which may be useful for heterojunction formation. The other *n*-type dopants that have been used successfully in CdTe are chlorine (Cl), bromine (Br), and iodine (I). Cl and Br appear to be very similar to In in terms of maximum donor concentration (N_D) ($2 \times 10^{18} \text{ cm}^{-3}$) and compensation.²³ ²⁴ For a comparison of common *n*-type dopants, these elements' maximum dopant density reported and activation energies in CdTe are given below in Tables 2 and 3, respectively.

The literature suggests that iodine is a promising alternative for *n*-type doping.²⁵ I doping of CdTe grown on (100)-oriented CdZnTe resulted in N_D as high as $6 \times 10^{18} \text{ cm}^{-3}$ without a Cd overpressure and without apparent compensation. Similar doping using conventional or metal-organic MBE on CdTe grown on (100)-oriented CdTe and (211)B-oriented GaAs substrates resulted in N_D as high as $3 \times 10^{18} \text{ cm}^{-3}$. I-doped CdTe samples made with ethyl iodide yielded extremely bright excitonic photoluminescence (PL) at 300 K, suggesting that these samples had fewer non-radiative defects.²⁵

Table 2. Maximum dopant density reported in literature.

Dopant	Max N_D in CdTe		Max N_D in CdZnTe			Max N_D in CdMgTe		
	N_D value (cm^{-3})	Ref	N_D value (cm^{-3})	% Zn	Ref	N_D value (cm^{-3})	% Mg	Ref
Ga	2.5×10^{16}	26	-	-	-	-	-	-
			-	-	-	-	-	-
In	2×10^{18}	27	1.2×10^{17}	0.1	28	-	-	-
			1.2×10^{16}	0.25	28	-	-	-
Cl	2×10^{18}	29	6×10^{16}	0.2	30	7×10^{15}	0.14	31, 32
			4×10^{15}	0.28	30	4×10^{15}	0.15	32
Br	1.8×10^{18}	23, 32	-	-	-	8×10^{17}	0.1	31, 32
			-	-	-	3×10^{15}	0.3	23, 31
I	6.2×10^{18}	28	1.2×10^{18}	0.1	28	1×10^{18}	0.22	32
			5×10^{17}	0.25	28	1×10^{17}	0.37	32

Table 3. Activation energies reported in literature.³³

	Activation Energy (meV)	Ref
Ga	13.88	34
In	14.15	34
	14.5	35
Cl	14.0	36, 37
	14.1	35
	14.48	34
Br	14.0	17
I	14	38

Although halogens can form hydrogen-like donors on the Te lattice sites, but elemental halogens are not compatible with the MBE process because of their high vapor pressures, hence the use of compounds like ZnC1_2 ,²⁹ ZnBr_2 ,³⁹ and tri-iodine-ethylene,⁴⁰ which have vapor pressures that are compatible with MBE. Although halogen compounds still have relatively high vapor pressures, the use of dual-zone low-temperature effusion cells ensures stable beam flux. Based on a review of the literature, ZnI_2 , which possess a vapor pressure comparable to that of Cd and Zn as given below in Figure 3, was chosen due to its ability to attain high doping concentration in CdTe as demonstrated in the literature. A dual-zone low-temperature effusion cell was used as the ZnI_2 source, and it

was constantly kept under the flow of chilled water to keep the temperature of the ZnI_2 material below 10 °C when not in use to limit sublimation and background I.

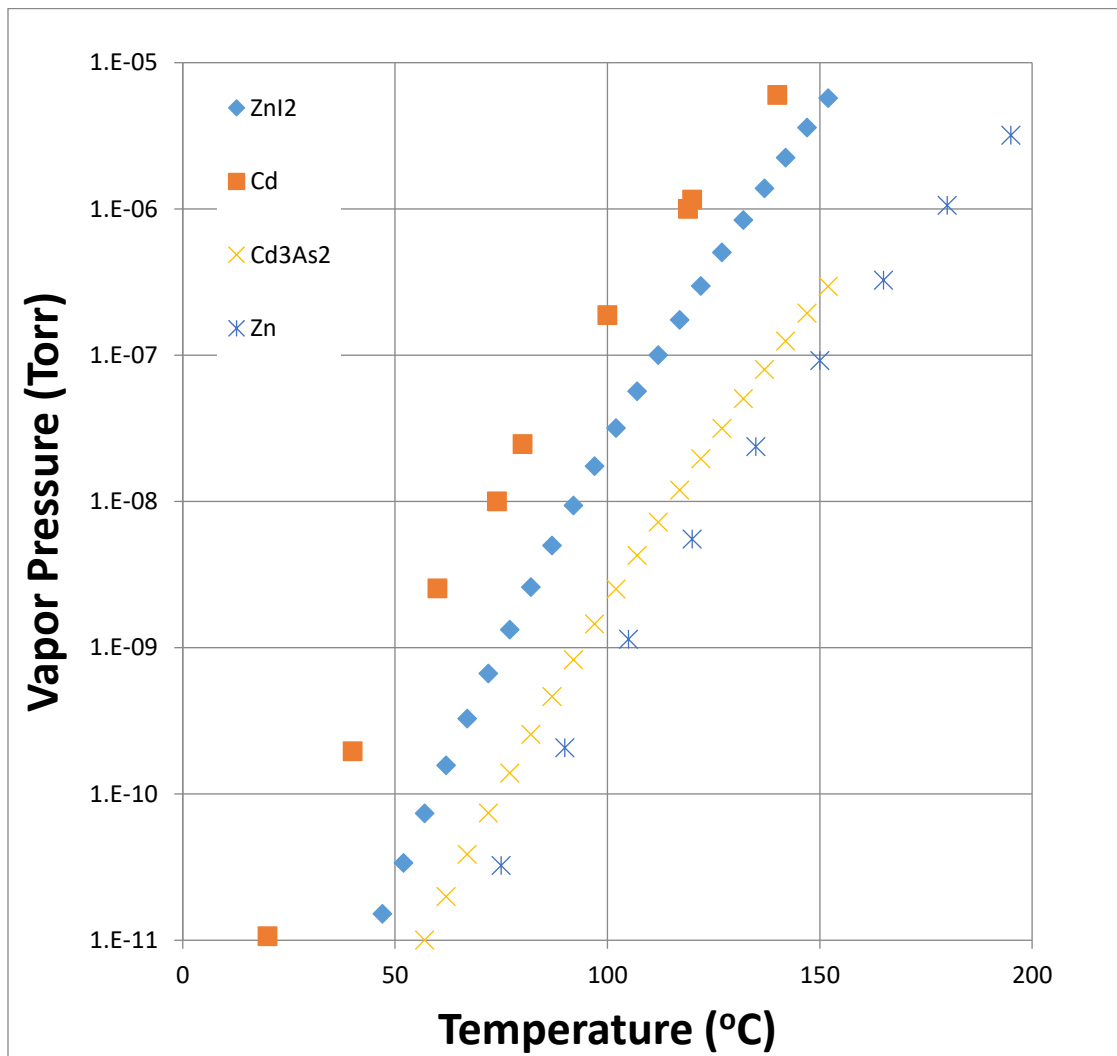


Figure 3. Vapor pressure curves for Cd, ZnI_2 , Cd_3As_2 , and Zn.

Generally, halogens are good dopants in CdTe ,¹⁷ but I in particular has been reported to be a more effective dopant when compared to Br and Cl. I doping achieves a higher free carrier concentration at room temperature than bromine³² and chlorine.⁴¹ Iodine doping with a gas source has yielded doping densities up to mid- 10^{18} cm^{-3} ,^{21, 28, 40} while use of the solid dopant source material ZnI_2 has yielded doping density up to

$7 \times 10^{18} \text{ cm}^{-3}$.³² Fischer et al.³² noted that, when doping density exceeds $1 \times 10^{19} \text{ cm}^{-3}$, compensation does occur. The major issue with iodine doping in CdTe is the natural formation of Cd-related vacancies that can pair with iodine, thereby leading to self-compensation.³³ The compensation mechanism tends to limit free-carrier concentration at this high doping density.³² Our research will focus on the limits and controllability of iodine doping in CdTe.

1.5 P-type Doping in CdTe

Cu, which can be substituted at Cd sites, can be used as a dopant in CdTe but results in low doping densities. Another major drawback of using Cu as a dopant in CdTe is that it can easily diffuse across the device junction, especially in CdS/CdTe, thereby degrading the performance of the solar cell device. Similarly, Ag is thermally unstable in CdTe due to its high diffusion coefficient. Most of group I, which are alkali metals that can also be substituted for Cd sites when used as dopants, have low activation energy but possess high diffusivity in CdTe and the tendency to occupy both Cd atomic sites (*p*-type) and interstitial positions (*n*-type), so achieving control of dopants becomes challenging.

Some of the group V elements, like N, P, As, Sb, and Bi, have been studied as potential candidates for *p*-type doping in CdTe via substitutional Te sites.¹⁷ When compared with Cu, most of these group V acceptor dopants have lower activation energies, as shown in Table 4.

Although N and P possess lower activation energies, N is not structurally stable when used as a dopant in CdTe, and P is reported to have fast grain-boundary diffusion,⁴² which will be problematic for production where polycrystalline CdTe is used. Arsenic

(As) is generally proposed as the choice acceptor dopant due to its relatively low activation energy and stability in CdTe. In comparing common p-type dopants, the maximum dopant density reported and activation energies in CdTe are illustrated below in Tables 4 and 5, respectively.

Table 4. Maximum dopant density reported in literature.

Dopant	Max N_A in CdTe		Max N_A in CdZnTe			Max N_A in CdMgTe		
	N_A value (cm^{-3})	Ref	N_A value (cm^{-3})	% Zn	Ref	N_A value (cm^{-3})	% Mg	Ref
Cu	4×10^{16}	43	-	-	-	-	-	-
			-	-	-	-	-	-
As	5×10^{16}	44	-	-	-	-	-	-
			-	-	-	-	-	-
P	5×10^{19}	45	-	-	-	-	-	-
			-	-	-	-	-	-
N	1×10^{16}	46	2×10^{17}	0.12	⁴⁷	1×10^{17}	0.1	⁴⁷
			2×10^{18}	0.5	⁴⁷	1×10^{17}	0.24	⁴⁷

Table 5. Activation energies reported in literature.³³

	Activation Energy (meV)	Ref
Cu	140	37
	146	37, 48, 49
	147	35
As	92	50
P	60	35
	68.2	48
	50	37
N	56	48, 49, 51
Na	58.1	35
	58.7	48
Ag	92	51
	107.5	49
	108	35
	123	37
Au	263	48

Arsenic has shown potential as a p-type dopant because it is a shallow acceptor,⁵⁰ and it has relatively low diffusion and segregation¹⁷ and good stability in the CdTe lattice,^{17, 52} however, it is still challenging to get acceptor concentration (N_A) as high as those seen in the n-type dopants of CdTe due to a low sticking coefficient, low activation at growth temperature,²⁰ and the need for post-growth annealing. Another challenge arises from the low growth temperature, which is required to have high As incorporation.²⁰ This can lead to poor crystal quality, and As can be incorporated into the defect sites.¹³ These issues make it challenging to achieve p-type doping in CdTe with high carrier concentration values without compromising the minority carrier lifetime.

Although post-growth annealing may be required for activation of As dopants in CdTe, this annealing improves crystal quality and activates the dopant,¹³ without degrading the doping profiles since As is stable in the lattice.⁵³

The use of a thermal cracker and an effusion cell has been investigated for incorporating As in MBE.¹⁹ The thermal cracker permits higher temperature growth and can be used to produce As₂,⁵³ which has a better sticking coefficient than As₄, making As₂ more desirable. To date, the use of a thermal cracker technique to achieve As doping mostly produced doping densities of 10^{17} cm^{-3} .^{13, 20, 54}

Shibli et al.¹⁹ used molecular-beam epitaxy (MBE) to grow ZnSe doped with As using two different sources—Zn₃As₂ and As cracker cell—as the As source. Shibli et al.¹⁹ studied different growth variations and their influence on As doping. They concluded that the As cracker yielded low dopant incorporation ($< 10^{17} \text{ atoms/cm}^3$) as compared to the Zn₃As₂ source, which yielded dopant incorporation that ranged from 10^{17} to $10^{21} \text{ atoms/cm}^3$. Near band-edge emission dominated by shallow acceptor levels was revealed in many Zn₃As₂ doped samples through low temperature photoluminescence. Cd₃As₂ will be used as the sister material to achieve As doping in CdTe. Cd₃As₂ is also compatible with MBE since its vapor pressure is comparable to the vapor pressures of Cd and Zn as shown in Figure 3. Similar to iodine doping studies, our research will focus on the limits and controllability of As doping in CdTe.

1.6 Technical Approach

The focus of this doping study is to understand how dopants interact in CdTe, including their limitations and how they can be controlled in such a way as to enhance device performance. The open-circuit voltage of most CdTe solar cell devices is currently less than $\sim 860 \text{ mV}$.⁵⁵ This research will focus on achieving open-circuit voltage $> 860 \text{ mV}$ in CdTe solar cells. The objectives of this research effort will be achieved through high carrier concentration ($N_A > 5 \times 10^{16} \text{ cm}^{-3}$ and $N_D > 5 \times 10^{17} \text{ cm}^{-3}$) while maintaining a

high carrier lifetime (τ values > 30 ns) in doped epitaxial layers grown by MBE for photovoltaic application. The effect of doping on carrier lifetime and carrier mobility will be studied. Efficient doping in CdTe will increase the V_{oc} levels in CdTe solar cells and subsequently increase the efficiency of CdTe solar cells. The thermal stability of these dopants against diffusion in CdTe will be examined. The knowledge gained from the doping studies will be a significant step toward better device performance in applications where CdTe doping is important. To achieve these goals, MBE growth of doped CdTe samples will be performed by varying the growth conditions in order to see how this affects dopant incorporation and subsequently determines optimal growth conditions for high N_A and N_D .

Some dopants in CdTe crystals are not electrically active at room temperature as incorporated. Examples of such dopants are As and P. High-temperature processing under cadmium ambient is needed for the dopant activation of As and P, which is being considered for the *p*-type side of a CdTe-based solar cell.⁵⁶ As previously mentioned, P is problematic for production, thereby necessitating that the focus of this research will be on As. The temperature annealing required for this activation will be performed in quartz ampoules. These ampoules will be cleaned with HF etchant before use, and ampoules will be sealed in a vacuum-tight environment. Annealing experiments will be done with and without Cd/Hg overpressure at temperatures above 400 °C to determine optimal conditions. The use of ampoule and tube furnace anneals will assist in shifting stoichiometry, fill vacancies, and activate dopants. Also, rapid thermal process (RTP) will be used for dopant activation. For effective study and analysis, several measurements will be made on the grown and annealed samples, including Hall measurement,

photoluminescence intensity measurements (PLI), confocal photoluminescence microscopy (cPL), atomic force microscopy (AFM), scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), time-resolved photoluminescence (TRPL), capacitance voltage measurements (CV), and secondary-ion mass spectrometry (SIMS). These characterization techniques will ultimately guide us in investigating carrier density and defect density in order to study the limits of doping, lifetime carriers, and mobility.

Due to the complexity and the delivery time of this project, I will perform MBE growth and characterize samples using AFM, confocal PL, XRD, spectral ellipsometry, and Hall measurements while contributing to PLI measurements and anneal experiments. TRPL measurements will be performed in Dr. Holtz's laboratory at Texas State University while SIMS measurements will be performed at EAG Laboratories in Sunnyvale, California, and device fabrication will be done at the National Renewable Energy Laboratory in Golden, Colorado.

2. EXPERIMENTAL EQUIPMENT

To achieve the research objectives and goals, several research tools were needed. Some of these tools included the MBE system itself, which was needed for the growth of the photovoltaic structures, the annealing station, which was needed to activate dopants after growth, and characterization tools, which were needed to evaluate the properties of the grown structures. Semiconductor characterization assists with the understanding and manipulation of the structural, thermal, optical, and electrical properties of thin-film materials and devices. The knowledge gained from the characterization process is essential in determining whether the semiconductor crystal is suitable for a particular device with certain functionalities. In this research endeavor, characterization was needed to determine the suitability of CdTe and CdTe-based alloys for photovoltaic application.

2.1 MBE System

In the early 1970s, MBE was developed to synthesize high-purity and high-quality semiconductor epilayers.⁵⁷ MBE is a technique used to develop thin epitaxial structures through the interaction of a molecular or atomic beam and the substrate surface. The substrate is kept at an elevated temperature during this process, and a high vacuum-evaporation apparatus is used in the system to keep the chamber pressure below approximately 10^{-11} Torr. The equilibrium vapor pressure of the elements and the semiconductor compound govern the MBE process.⁵⁸ Due to the low-pressure environment, the growth temperature is relatively low and minimizes undesired thermal activity. The advanced epitaxial technique also allows for precise control of thickness and dopant concentration, enabling growth of almost all II-VI compounds.⁵⁹ The compositional make-up of the MBE-grown epilayer depends on the arrival rate of the constituent elements

and is contingent upon the evaporation rate of the atomic or molecular sources.

2.1.1 Growth chamber

The stainless steel MBE system at Texas State University, as shown in Figure 4, consists of seven growth chambers, an atomic-hydrogen cleaning chamber, an XPS chamber, a scanning probe microscopy (SPM) chamber, two load-lock chambers, and buffer chambers. The growth chambers of this multi chamber MBE system are made up of a II-VI chamber, IV-VI chamber, As-based chamber, Sb-based chamber, and three oxide chambers.

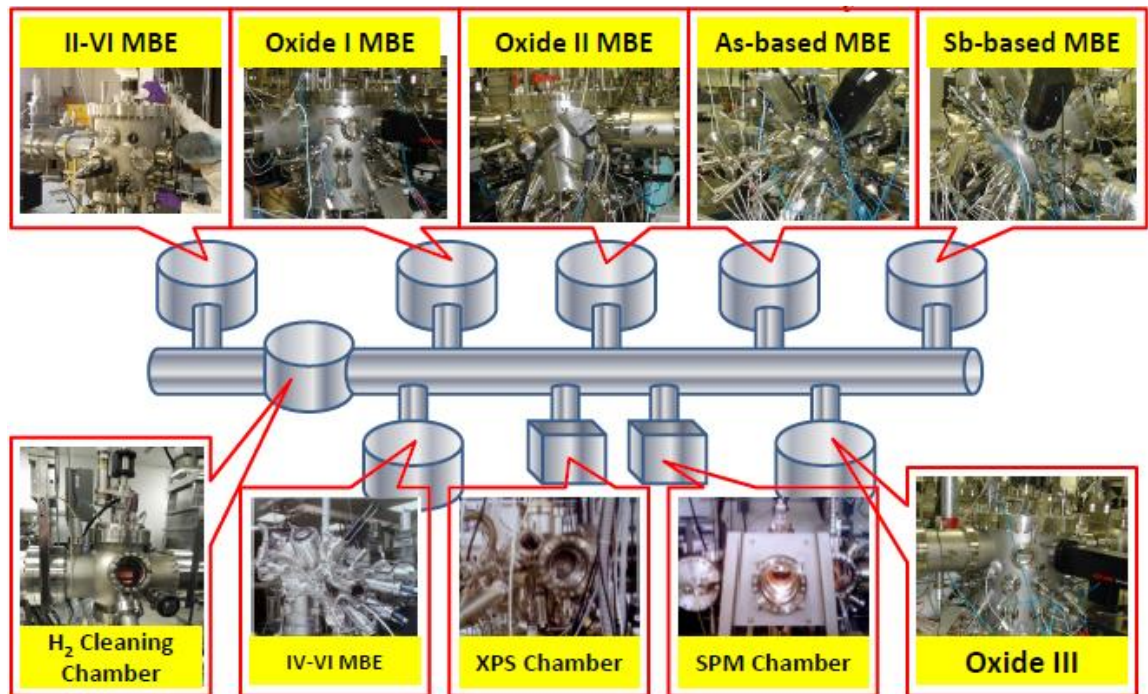


Figure 4. MBE growth and characterization system at Texas State University showing the II-VI MBE, Sb-based MBE, and hydrogen-cleaning chamber that were used for this project.

Of the seven chambers in this multi-chamber MBE system, the II-VI chamber, Sb-based chamber, and hydrogen-cleaning chamber were the chambers used for this

project. Two load-lock chambers and buffer chambers were built into this multi-chamber MBE system to load, prepare, transfer, and temporarily hold samples. All the chambers are isolated with gate valves, and all chambers have pumps to keep them under vacuum. The most important aspect of MBE growth takes place in the growth chamber. The II-VI growth chamber grew all the samples used in this project. The Sb-based chamber deposited an InSb buffer layer on InSb substrates before growing CdTe-related structures for specific experiments. The basic components of the II-VI growth chamber at Texas State University are the shutters, substrate manipulator and substrate heater, ion pump, cryo pump, effusion cells, ion gauge beam flux monitor (BFM), and reflection high-energy electron diffraction (RHEED), which is further described in section 2.2. A schematic diagram of a typical MBE growth chamber is shown in Figure 5.

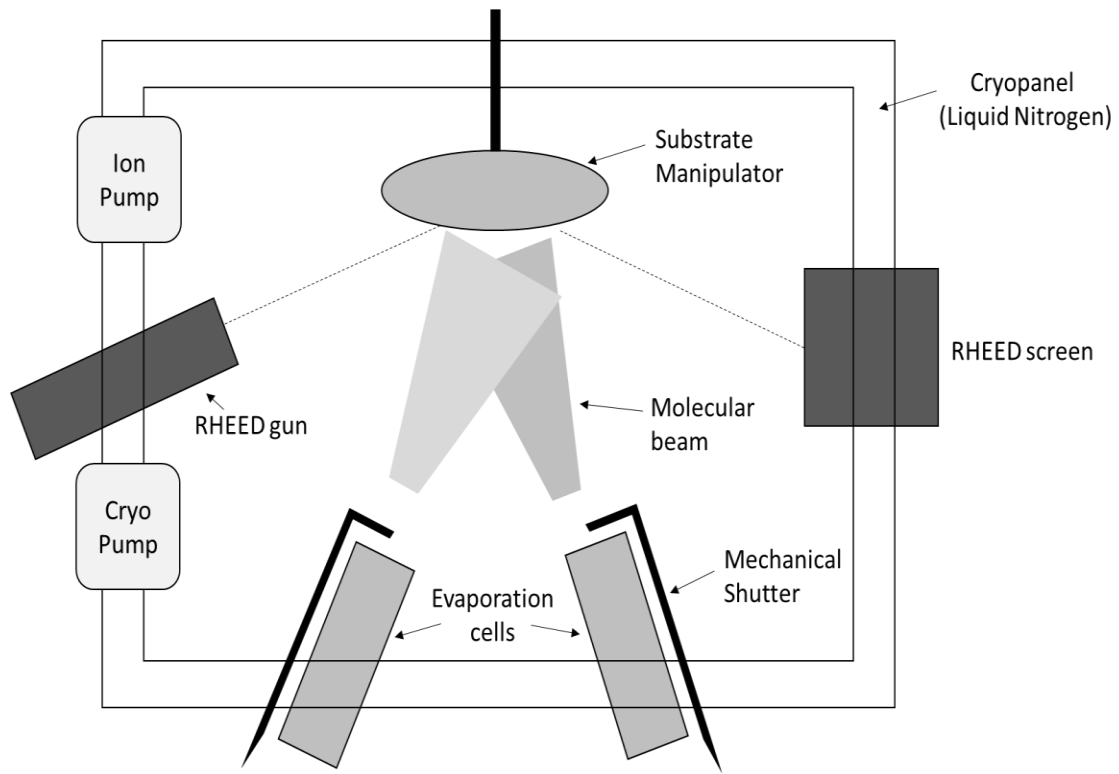


Figure 5. Schematic diagram of a typical MBE growth chamber.

Typical base pressure in the growth chamber ranges between 10^{-10} Torr and 10^{-11} Torr. The growth chamber attains this pressure range with the aid of the pumping system—ion pump and cryo pump—that pumps out residual impurities, and the liquid nitrogen cryopanel, which surround the main chamber wall and the source flange. This liquid nitrogen shroud assists in trapping materials with excess high vapor pressure and thermally isolates material sources.

2.1.2 Sources

A key goal in film deposition using MBE is to control the composition and uniformity of the deposited material in order to achieve quality growth. Effusion cells provide molecular beams, which enable controlled material deposition in the MBE system. Some of the key considerations in the design of such sources are material purity, good flux stability, and uniformity. There were two types of sources used in this project: conventional effusion sources and dissociation effusion sources.

2.1.2.1 *Conventional effusion source*

Effusion cells used in this project were low-temperature dual filament sources purchased from Veeco Inc. These effusion cells have crucibles that hold source material in condensed forms. These cells were heated through radiation generated from a heat-resisting source, which is usually Tantalum (Ta). The temperature of these cells was stabilized with Eurotherm 818 temperature controllers and feedback loops. A properly controlled temperature usually leads to stable and uniform flux from the source material. Compound CdTe was used as the primary source material while Cd was used to provide

excess Cd during CdTe layer growth in order to limit defect formation in growing CdTe layers.⁶⁰ These source materials used effusion cells. Other source materials that used effusion cells in this project are Zn, Cd₃As₂, ZnI₂, and Mg.

2.1.2.2 *Dissociation (cracker) effusion source*

The cracker cell is a modified design of the conventional effusion cell. The molecular beam emanating from the Knudsen-type crucible is guided through a higher temperature (cracker) zone in the source so that tetrameric molecules, as seen in some group V materials—especially As₄ and P₄—dissociate into dimers. Dimers are believed to have a higher sticking ratio than the tetramers. For most of this study, arsenic doping of CdTe was performed using a conventional effusion cell. A custom-made cracker (discussed in section 4.3.1) was introduced in the later part of the research process to increase the As incorporation in CdTe crystals. A cracker was also used to obtain atomic hydrogen from molecular hydrogen, which was then used to prepare sample surfaces before growth.

2.1.3 Ion gauge beam flux monitor

The BFM primarily consists of a moveable ion gauge that can be moved into and out of the position the substrate will occupy during growth. The molecular beam flux of a material is measured when the BFM moves into the substrate position and the shutter of the material is opened for a brief period, which occurred for approximately two minutes for the materials used in this project. The pressure measurement taken when the shutters of the cells are closed is referred to as the base pressure. The beam equivalent pressure (BEP) of the incident molecular flux emanating from the source is determined by

subtracting the base pressure from the pressure reading obtained from the BFM when the source shutter is open. Information about the BEP of individual constituents within a compound semiconductor is essential in maintaining the stoichiometry needed for the growth of the compound material, which necessarily has specific, desirable properties. The ion gauges that measure these BEPs are calibrated to measure the partial pressure of nitrogen. The rate at which the molecules in nitrogen will ionize is different from the rate at which the molecules in other materials will ionize when using these ion gauges, thereby making the BEP values obtained for other materials different from the actual partial pressures of these other materials. In order to determine the actual flux measurement, the measured BEP value will have to be adjusted with a sensitivity factor relative to nitrogen. This relative sensitivity is known as ionization efficiency. Flaim et al.⁶¹ provided the experimental ionization efficiencies relative to nitrogen. The mathematical expression for these ionization efficiencies is given as ⁶²

$$n_i = \frac{0.6Z_i}{14} + 0.4 \quad (2.1)$$

where n_i is the ionization efficiency of the molecule relative to nitrogen and Z_i is the number of electrons in the element. The ionization efficiency of Cd, Te, and CdTe are calculated below.

For Cd, $Z_{Cd} = 48$

$$n_{Cd} = \frac{0.6Z_{Cd}}{14} + 0.4 = 2.457 \quad (2.2)$$

For Te, $Z_{Te} = 52$

$$n_{Te} = \frac{0.6Z_{Te}}{14} + 0.4 = 2.629 \quad (2.3)$$

For Te_2 , $Z_{\text{Te}_2} = 104$

$$n_{\text{Te}_2} = \frac{0.6Z_{\text{Te}_2}}{14} + 0.4 = 4.857 \quad (2.4)$$

The flux (J) ratio of two substances are related to the cell temperatures (T), molecular weights (M), ionization efficiencies (n), and the beam equivalent pressure (B) of these substances. This relationship is given as ^{62, 63}

$$\frac{J_x}{J_y} = \left(\frac{B_x}{B_y} \times \frac{n_y}{n_x} \right) \times \sqrt{\left(\frac{M_y}{M_x} \times \frac{T_x}{T_y} \right)}. \quad (2.5)$$

For CdTe, which dissociates as follows



the flux ratio can be written as

$$\frac{J_{\text{Cd}}}{J_{\text{Te}_2}} = \left(\frac{B_{\text{Cd}}}{B_{\text{Te}_2}} \times \frac{n_{\text{Te}_2}}{n_{\text{Cd}}} \right) \times \sqrt{\left(\frac{M_{\text{Te}_2}}{M_{\text{Cd}}} \times \frac{T_{\text{Cd}}}{T_{\text{Te}_2}} \right)}. \quad (2.7)$$

Also, from the dissociation, the flux ratio can be derived as

$$\frac{J_{\text{Cd}}}{J_{\text{Te}_2}} = 2 \quad (2.8)$$

assuming

$$T_{\text{Cd}} = T_{\text{Te}_2} = T_{\text{CdTe}}. \quad (2.9)$$

Molecular weights are given as

$$M_{Cd} = 112.411 \text{ g/mol}$$

$$M_{Te2} = 255.20 \text{ g/mol}$$

$$M_{CdTe} = 240.011 \text{ g/mol}$$

The values for flux ratio, temperature, molecular weight, and ionization efficiency can be substituted in equation 2.7.

$$2 = \left[\left(\frac{B_{Cd}}{B_{Te2}} \right) \times \frac{4.857}{2.457} \right] \times \sqrt{\left(\frac{255.20 \text{ g/mol}}{112.411 \text{ g/mol}} \times 1 \right)} \quad (2.10)$$

$$2 = \left[\left(\frac{B_{Cd}}{B_{Te2}} \right) \times 1.977 \right] \times \sqrt{2.27} \quad (2.11)$$

$$2 = \left(\frac{B_{Cd}}{B_{Te2}} \right) \times 1.977 \times 1.507 \quad (2.12)$$

$$2 = \left(\frac{B_{Cd}}{B_{Te2}} \right) \times 2.979 \quad (2.13)$$

$$0.67 = \left(\frac{B_{CdTe}}{B_{Te2}} \right) \quad (2.14)$$

$$\frac{B_{Cd}}{B_{Te2}} = 0.67 \quad (2.15)$$

$$B_{Cd} = 0.67 B_{Te2} \quad (2.16)$$

$$B_{Te2} = 1.49 B_{CdTe} \quad (2.17)$$

2.2 Reflection High-Energy Electron Diffraction

RHEED uses a high-energy beam of electrons of about 5 keV – 40 keV focused on a sample surface at a low incidence angle of about 1°-3° in order to obtain structural

information by minimally penetrating the few outermost atomic layers of the sample surface. The beam reflection is seen on the RHEED screen.

The basic setup of the RHEED experiment as shown in Figure 6 consisted of the RHEED assembly, the sample, the display screen, and a charge-coupled device (CCD) camera. The display screen used for this work is a phosphor-coated screen. A charge-coupled device (CCD) camera is located behind the display screen right outside of the MBE chamber to view and record the diffracted patterns. In most cases, samples were rotated about their normal axes to align the incident electron beam with specific crystallographic directions on the surface before diffracted patterns were recorded. These patterns give information about crystal pattern and growth quality, which was used as a feedback mechanism to optimize growth conditions during and after growth occurred.

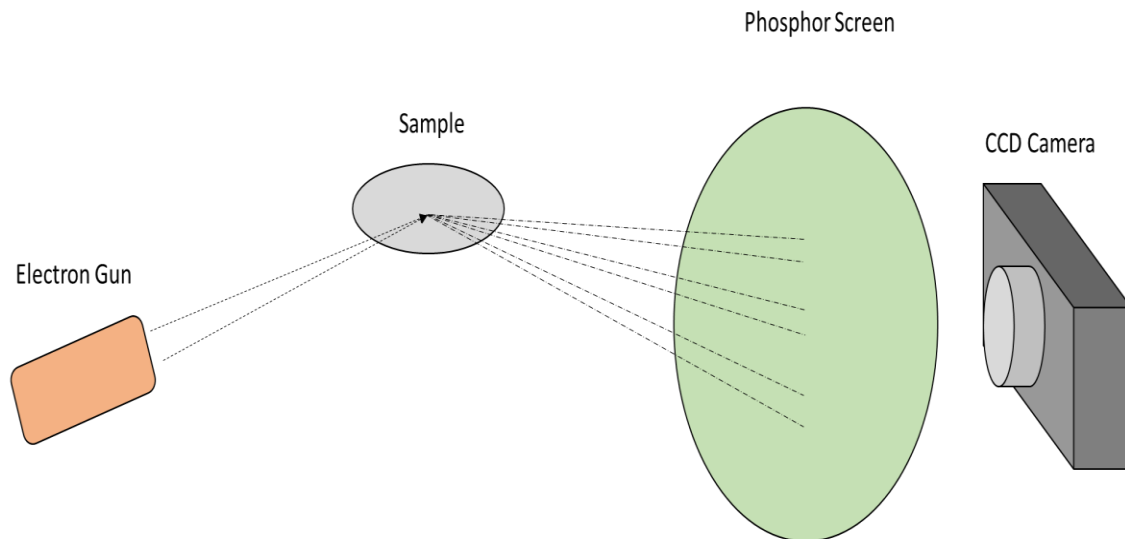


Figure 6. Schematic drawing of the RHEED measurement showing the electron gun, the sample, the phosphor screen, and the CCD camera.

RHEED, as a useful analytical technique in MBE growth, helps in real-time monitoring of the crystal structure for the film being grown. RHEED patterns provide information about the texture of the surface, i.e. either smooth or rough. The diffraction process on smooth surfaces is usually characterized by elongated streaks that are a result of true reflection diffraction. The diffraction process on rough surfaces is characterized by spotty features resulting from transmission-reflection diffraction.

In this project, RHEED was used to provide information about the surface topography and the precise growth rate. Atomic-force microscopy (AFM) was used to correlate RHEED surface characterization in this research study.

2.3 Atomic-Force Microscopy

AFM is a type of scanning probe microscope that measures the interaction force between the tip and the sample surface as shown in Figure 7. The tip is located at the free end of a cantilever that is 100 to 200 μm long. Forces between the tip and the sample surface cause the cantilever to bend or deflect. The movement of the cantilever is influenced by the sample surface, which is detected by selective sensors. The major factors that determine the interaction force are the AFM probe tip, the nature of the sample, and the distance between them.⁶⁴ This technique is useful in studying the surface morphology of a specimen.

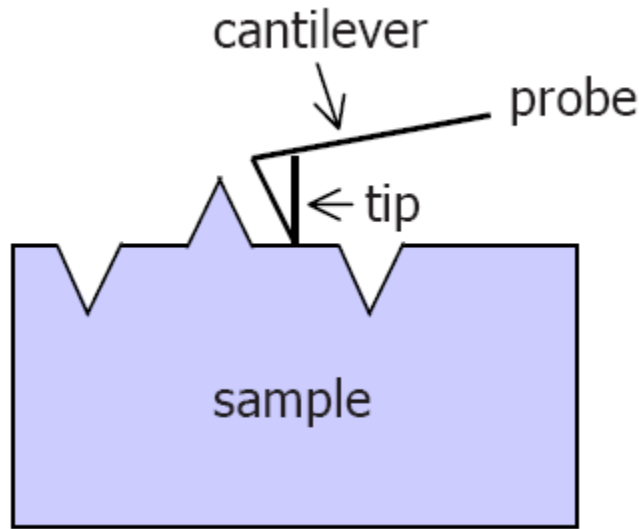


Figure 7. Schematic of an AFM tip scanning over the surface of a sample.⁶⁴

The Veeco Dimension 3100 AFM at Texas State University used in this research study operates in both contact and non-contact (tapping) modes. The tips used by this AFM are generally less than 100 Å in diameter and a few microns in length. High-resolution topographic images were obtained for this study using the AFM in tapping mode where sample surface scanning is achieved by the tip coming into contact with the surface and lifting off at very small spatial intervals over the scanned area.

2.4 Hall Effect

Hall measurement is a technique that can be used to extract information about electrical properties such as carrier concentration, mobility, and resistivity from a conductor or semiconductor. This technique is based on the application of small transverse voltage across a current-carrying material under an applied magnetic field.

The Hall effect is based on generating voltage from the Lorentz force. A magnetic force occurs when a magnetic field is applied to a charge moving along an electric field whose direction is perpendicular to the magnetic field. This Lorentz force F is given as

$$F = -q(E + (v \times B)) \quad (2.18)$$

where q is the elementary charge, E is the electric field, v is the particle velocity, and B is the magnetic field.

As current I flows across the conducting material, and a perpendicularly directed magnetic field is applied, electrons tend to drift away from the direction of the current while holes move in the same direction as the electric force, thereby resulting in an excess electric charge building up perpendicular to the direction of the current, hence a potential drop. This transverse voltage, known as Hall voltage, is given as

$$V_H = IB/qnd \quad (2.19)$$

where I is the current, B is the magnetic field, d is the sample thickness, n is the bulk density of charge carriers in a semiconductor, and q is the elementary charge. With $nd = n_s$, equation 2.19 can be written as

$$V_H = IB/q n_s \quad (2.20)$$

The mobility μ and the sheet density n_s of a material with an arbitrary shape can be determined with the combination of Hall measurement and resistivity using the van der Pauw technique. This technique is convenient in that four small ohmic contacts can be placed at the edges of the arbitrarily shaped sample. A typical example of a van der Pauw configuration for a square-shaped conducting material is shown in Figure 8. I is applied across two opposing contacts (3 and 4) of this sample while V_H is measured across the

remaining two opposing contacts (1 and 2) as a constant magnetic field B is applied in a direction perpendicular to the plane of the material.

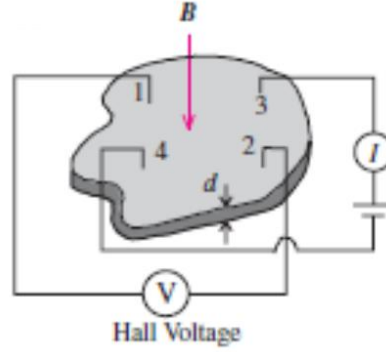


Figure 8. Van der Pauw configuration for a arbitrarily shaped conductor.⁶⁵

The Hall coefficient in this van der Pauw configuration is given as

$$R_H = \frac{[V_{12}(B) - V_{12}(0)]d}{I_{34}B} = \frac{[V_{12}(B) - V_{12}(-B)]d}{2I_{34}B} \quad (2.21)$$

where d is the thickness of the sample and B is the magnetic field. The resistivity (ρ) of the sample can also be measured through this van der Pauw method by measuring the voltage drop across two contacts and, then, measuring current I across the remaining two contacts using different contact configurations. The resulting resistances are given as

$$R_{12,43} = \frac{|V_{12}|}{I_{43}} \quad (2.22)$$

$$R_{23,14} = \frac{|V_{23}|}{I_{14}} \quad (2.23)$$

$$R_{34,21} = \frac{|V_{34}|}{I_{21}} \quad (2.24)$$

$$R_{41,32} = \frac{|V_{41}|}{I_{32}} \quad (2.25)$$

The resistivity is then given as⁶⁶

$$\rho = \left[\frac{\pi d}{\ln 2} \times \frac{1}{4} \times \left(\frac{V_{12}}{I_{43}} + \frac{V_{23}}{I_{14}} + \frac{V_{34}}{I_{21}} + \frac{V_{41}}{I_{32}} \right) \right] \Omega - \text{cm}, \quad (2.26)$$

and the Hall mobility is given as ⁶⁶

$$\mu_H = \left[\frac{10^8}{B} \times \frac{\ln 2}{\pi} \times \frac{2(V_{1324} + V_{2413})}{(V_{1243} + V_{2314} + V_{3421} + V_{4132})} \right] \frac{\text{cm}^2}{\text{V s}} \quad (2.27)$$

while the charge carrier density is given as ⁶⁶

$$n_H = \left[6.25 \times 10^{10} \times \frac{B}{d} \times \frac{1}{2} \times \left(\frac{I_{24}}{V_{13}} + \frac{I_{13}}{V_{24}} \right) \right] \text{cm}^{-3} \quad (2.28)$$

Van der Pauw Hall measurements were made using a Physical Property Measurement System (PPMS) at Texas State University. This PPMS, manufactured by Quantum Design, is shown below in Figure 9. Its major components are an EverCool model dewar, probe, model 6000 PPMS controller, electronics cabinet, vacuum pumps, and sample puck.



Figure 9. The PPMS setup at Texas State University.

This PPMS permits a selection of electrical, magnetic, and optical measurements to be performed in variable-temperature and variable-magnetic field environments. These measurements can be done at temperatures varying from 1.9 K to 310 K with magnetic fields varying from -9 to 9 Tesla.

Samples used in the Hall measurements were carefully designed and prepared for this purpose. Uniform thin films with known thicknesses were grown on non-conducting substrates. Ohmic contacts were prepared by melting indium and adding droplets—they were exceptionally small relative to the size of the sample—to the four corners of the sample. Samples were mounted on an AC Transport Puck with rubber cement, and the contacts of the samples were connected to the AC Transport Puck via Au wires to achieve van der Pauw configuration. The use of the PPMS ensured a uniform temperature to avoid thermomagnetic effects on the measurements.

Variable temperature measurements were performed in order to determine the temperature dependence of the carrier concentration in some select samples.

2.5 Capacitance-Voltage Measurements

The C-V measurement method can be used to estimate the carrier concentration of dopants as a function of depth. This method of estimating carrier concentration is based on the depletion approximation where it is assumed that the depletion region (also known as the space-charge region) of the device being measured is void of free carriers. It is also assumed that other regions in the device are neutral while the transition between the depletion and the neutral regions is expected to be abrupt.

In a typical, metal-to-n-type semiconductor junction, the n-type carrier concentration, which is assumed to be homogenous and uncompensated, can be obtained from the following relations.⁶⁷

$$N = \frac{-2}{A^2 \epsilon_0 \epsilon_r q} \left[\frac{d(1/C^2)}{dV} \right]^{-1} = \frac{C^3}{q \epsilon} \frac{dV}{dC} \quad (2.29)$$

where C is the capacitance, ϵ_0 is the permittivity of a vacuum, ϵ_r is the dielectric constant of the semiconductor, A is the area, q is the electron charge, and V is voltage.

$$C = \frac{\epsilon_0 \epsilon_r}{W_D} A \quad (2.30)$$

where W_D is the depletion width.

The depletion width can be extracted from the capacitance measurement at any voltage value, and the slope of the plot of $1/C^2$ vs. V can be used to extract the carrier concentration. Also, the local derivative of $1/C^2$ vs. V at any given voltage can be used to extract the carrier concentration in the non-uniform doping case. This method is also valid for determining hole concentration.

2.6 Secondary Ion Mass Spectrometry

Secondary ion mass spectrometry (SIMS) is an effective tool for measuring the isotopic, molecular, or elemental composition of samples. Its ability to detect all elements, unlike XPS, and its ability to detect small concentration makes SIMS extremely useful in doping studies.

The basic components of SIMS experiments, as shown in Figure 10, compose the primary particle source, which is used to generate secondary ions from the sample surface, the mass spectrometer, and an ion detection system.

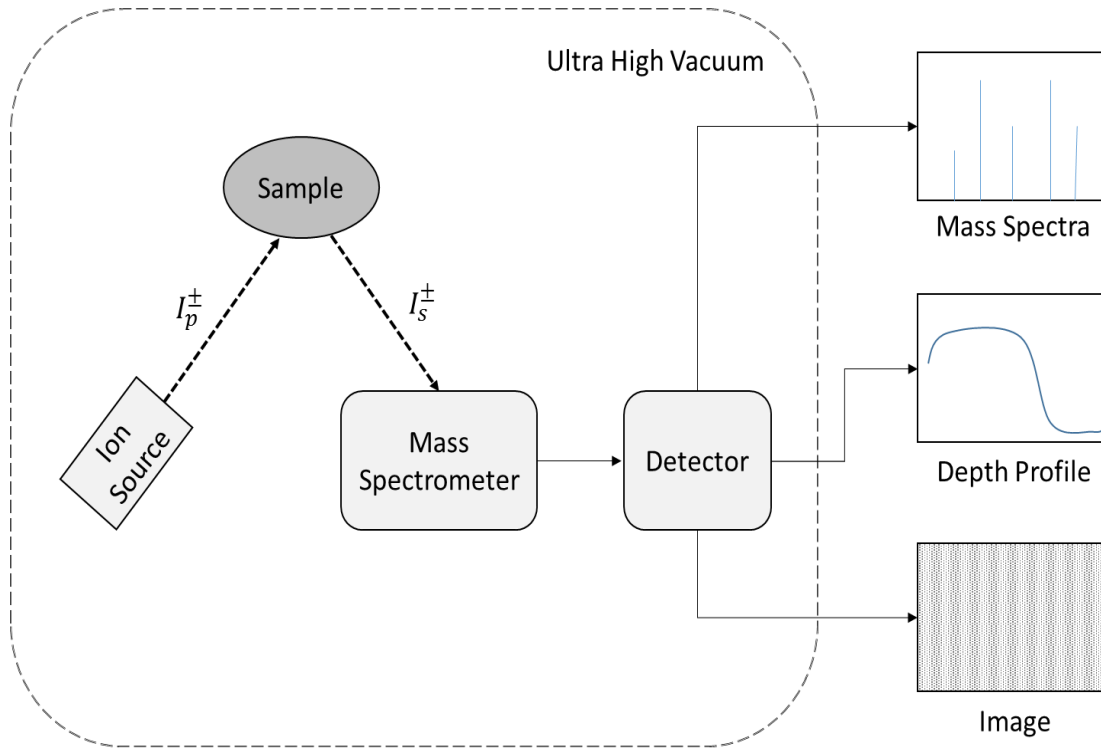


Figure 10. A schematic representation of a SIMS instrument.

In SIMS, the surface of the sample analyzed is inundated by high-energy (usually less 50 keV) beam of ions, transferring its energy to the atoms of the solid through multiple collisions and causing atoms near the surface to escape from the sample. Some of these atoms escaping the sample surface, referred to as secondary particles, are ionized in this emission process. Ionized particles present in the secondary particles are collected and analyzed by a mass spectrometer.

SIMS has great applications in depth profiling, where the elemental composition of a sample is measured as a function of depth. This technique, known as dynamic SIMS, destroys the sample surface, but it is more accurate than static SIMS where surface destruction is less intensive. Static SIMS uses a rather low primary flux density, so there is no significant sputter etch unlike dynamic SIMS, which uses a higher primary flux density to achieve a sputter crater in the sample over a period of time. Surface damage is minimized in static SIMS, but secondary ions are low, thereby requiring detectors that are more sensitive. In static SIMS, the secondary ions analyzed can provide information about the chemical profile of the surface because each point within the scanned surface is impacted by the primary particle once, on average.

SIMS measurements for this research study were conducted at EAG Laboratories where elements in the CdTe matrix were measured using a PHI Quadrupole SIMS instrument. Standards were created with ion-implanted samples. The detection limits of some elements in CdTe under the depth profiling condition are shown in Table 6, which ranges from 10^{12} atoms/cm³ to 10^{16} atoms/cm³. The depth resolution is approximately 5 Å while the lateral resolution for depth profiling is up to 10 µm.

Table 6. SIMS detection limits of selected elements in CdTe under normal depth profiling conditions.

O₂⁺ Primary Ion Beam Positive Ions		Cs⁺ Primary Ion Beam Negative Ions		Cs⁺ Primary Ion Beam Positive Ions (CsM⁺)	
Element	Detection Limit (atoms/cm³)	Element	Detection Limit (atoms/cm³)	Element	Detection Limit (atoms/cm³)
Al	1E12	As	1E15	As	2E14
Mg	3E12	Br	5E13	Zn	2E15
Zn	2E16	C	1E15		
		Cl	1E14		
		F	5E13		
		I	5E12		
		O	5E15		
		S	1E14		

SIMS measurements from EAG Laboratories were mainly depth profiles used to determine the concentration of dopants and impurities in CdTe crystal. A scan of some impurities in one of the CdTe samples grown at Texas State University is shown in Figure 11.

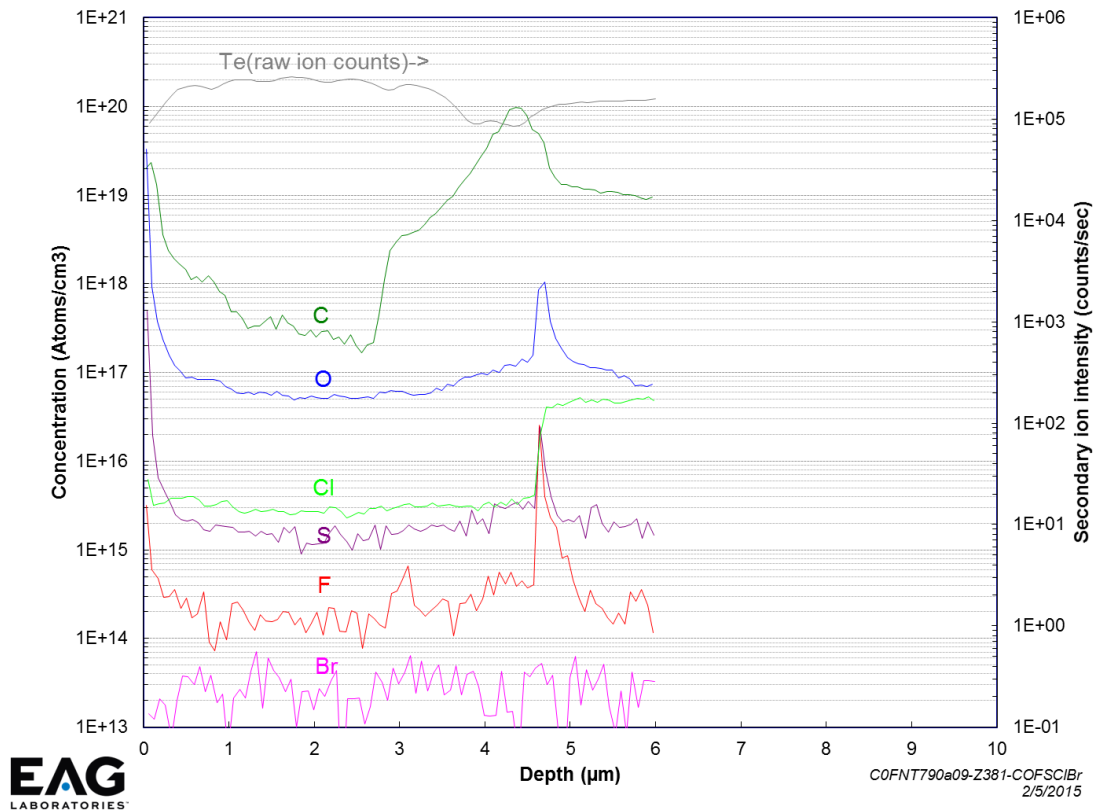


Figure 11. A SIMS depth profile showing the concentration of impurities in a CdTe sample.

2.7 Confocal Photoluminescence Microscopy

Confocal photoluminescence microscopy (cPL) is a technique that combines lateral resolution with optical sectioning capability. This tool has been used in the field of biology and engineering, and it is currently being applied to semiconductors in a way that reveals the defect density present in the crystal structure.⁶⁸ The image formation of a typical confocal optical system is compared to a typical image formation optical system in Figure 12. The major difference in these optical systems is the confocal pinhole aperture.

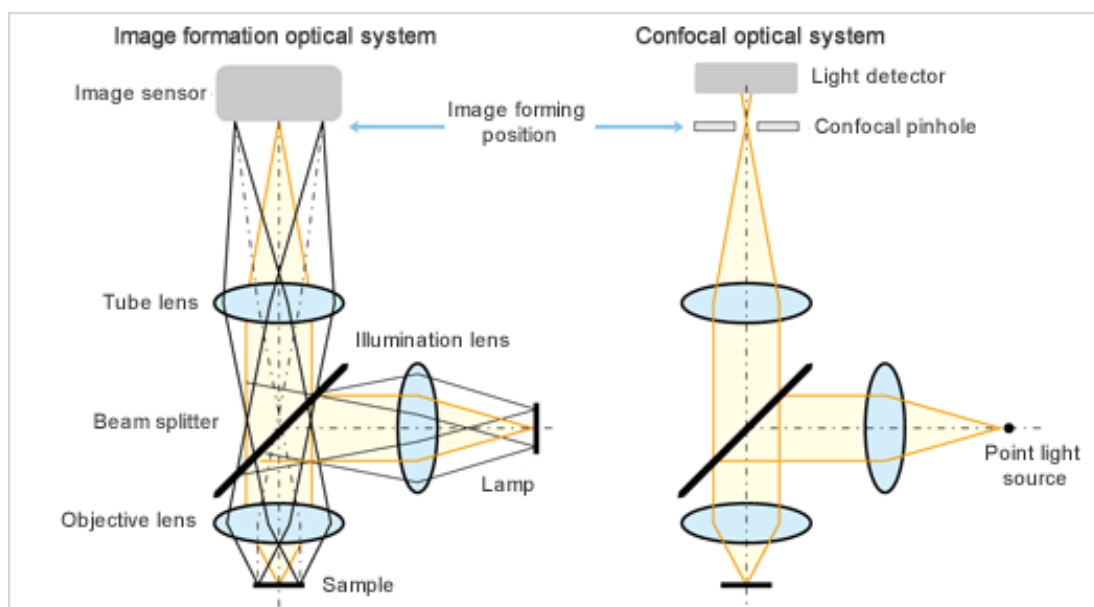


Figure 12. Image formation optical system and confocal optical system for optical microscopes.⁶⁹

The confocal optical system uses a confocal pinhole to allow the passage of light that is in focus at the aperture while filtering out light that is not. In most confocal optical systems, laser lights with a specific wavelength are used to emit light, which is then converged to a point on the sample with the help of an objective lens. The light reaching the sample generates photoluminescence. This photoluminescence travels back through the objective lens and the beam splitter before it converges on the pinhole to form a focused, clear image with sharp contrast. As photoluminescence is being collected, reflected laser light is filtered with the help of beam-path filters. This setup enables the creation of a non-radiative defect map of the sample that is measured.

The confocal PL measurements done at Texas State University were performed using the Olympus FV1000 Laser Scanning Confocal Microscope setup shown in Figure 13.



Figure 13. Confocal PL setup with Olympus FluoView™ FV1000 Laser Scanning Confocal Microscope at Texas State University.

This confocal PL setup achieves $0.25\ \mu\text{m}$ lateral resolution and $0.25\text{-}0.5\ \mu\text{m}$ depth resolution. It has multi-line argon lasers (515, 488, and 458 nm) and diode lasers (405, 559, and 635 nm). The FV1000 Laser Scanning Confocal Microscope has a motorized upright microscope and a light detector that can be used for bright-field or DIC imaging. Confocal PL was used to obtain images that provided information about the types and quantity of defects present in the MBE-grown CdTe based samples.

2.8 Photoluminescence Intensity measurements

The photoluminescence intensity (PLI) measurement is a nondestructive, contactless technique for characterizing electronic properties of a material where the

intensity of the emitted light from the band edge is monitored at a particular wavelength corresponding to the band-gap energy. To generate photoluminescence in samples, a monochromatic light is used to provide excitation energy, and then a power meter is used to measure the excitation. The photoluminescence intensity is directly proportional to the radiative recombination rate at a particular depth and it is given as ⁷⁰

$$PLI \propto Re^{-\alpha d} \quad (2.31)$$

where d is the depth, α is the absorption coefficient at the excitation wavelength, and R is the radiative recombination rate. The PLI measurement setup at Texas State University is shown in Figure 14.

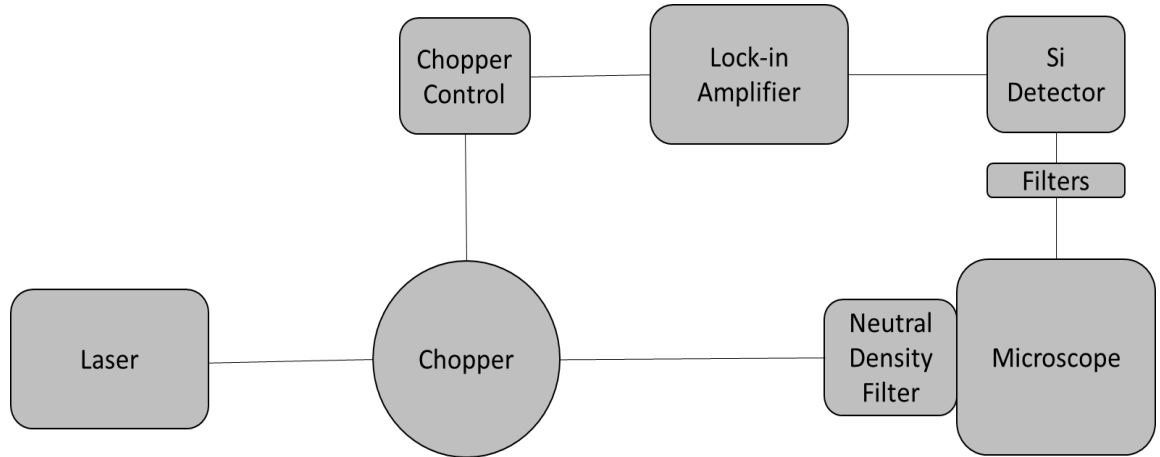


Figure 14. Block diagram for the PLI setup at Texas State University.

A Coherent INNOVA 90 laser was used to provide excitation light with a wavelength of 514 nm, which was chopped at 400 Hz using a Stanford Research Systems Model SR540 chopper controller. This chopped light passes through a set of neutral density (ND) filters to control the excitation intensity before it goes through a 6.5x objective lens, which focuses the laser light onto the microscope's stage to generate photoluminescence from the sample. The photoluminescence generated passes through

this same objective lens while reflected laser light is filtered out. The photoluminescence passing through the objective lens focuses on a ThorLabs Si Amplified photodiode detector, which sends a voltage response to a Stanford Research Systems Model SR830 DSP lock-in amplifier. Calibrated ND filters were used to vary the laser intensity, and the output intensities were recorded.

2.9 Time-Resolved photoluminescence

Time-resolve photoluminescence (TRPL) was used to measure carrier lifetime in this research project, as it is a parameter of interest in photovoltaic devices. TRPL provides useful information about carrier recombination processes that follow charge carrier relaxation in semiconductors like CdTe. The observed lifetime (τ_{ob}) consists of radiative lifetime (τ_r) and non-radiative lifetime (τ_{nr}). The relationship between the lifetimes is given as ^{71, 72}

$$\frac{1}{\tau_{ob}} = \frac{1}{\tau_r} + \frac{1}{\tau_{nr}} \quad (2.32)$$

TRPL involves using a pulsed- or on/off-modulated light source for excitation at a given wavelength and then measuring and recording the resulting time profile of the PL. Most TRPL setups typically have a pulsed laser source for excitation and a photodiode, streak camera, or photomultiplier tube (PMT) for PL detection. There are several TRPL measurement techniques, but they all share similar a process of gaining excitation through a pulsed- or on/off-modulated light source and recording the PL while the excitation source is off.⁷³ Some of these techniques are time-correlated single photon counting (TCSPC), photoluminescence upconversion (PLU), and streak cameras. TCSPC is a relatively simple and versatile technique, making it one of the most widely used

TRPL techniques, but it can be limited by the resolution of the detector.⁷² The schematic diagram of a typical time-correlated single photon counting (TCSPC) TRPL system is shown in Figure 15. This technique is designed for detecting a single photon during each excitation pulse.

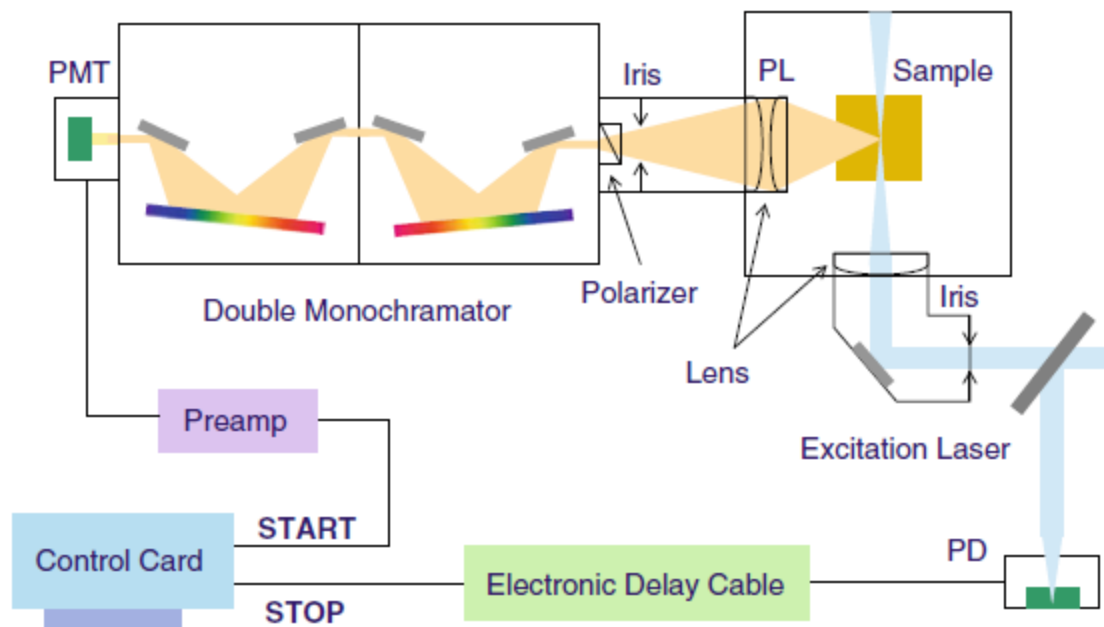


Figure 15. The schematic diagram of a typical TCSPC TRPL system.⁷⁴

For this project, TRPL was measured by time-correlated single photon detection at Dr. Holtz's laboratory at Texas State University as Dr. Sohal used a 640 nm or 430 nm pulsed laser, which focused on a spot size of about 800 μm to give an injection level of 7×10^9 photons/ cm^2 for a pulse.

2.10 X-Ray Diffraction

XRD is ideally suited to probe crystal-lattice structures. Wave diffraction occurs when the dimensions of the diffracting object are of the same order of magnitude as the wavelength of the incident wave. A diffractometer consists of an X-ray tube in which an

accelerated electron beam (up to 30 keV) impinges on a water-cooled copper target to generate the X-rays. The generated X-rays are filtered and aligned by using a monochromator.

Diffraction depends on the interference of waves originating from the same source but taking different paths to the same point. The difference in phase between waves is dependent only on the effective path length, neglecting the fact that waves arriving at the same point at the same time were emitted by the source at different times. Since the phases are time dependent, waves emitted by the source at times that are too far apart can no longer form a constant interference pattern. The length over which the phases correlate is referred to as coherence length. The path-length difference must be smaller than the coherence length before interference can occur.

Diffacted waves from different atoms can interfere with each other, and the intensity distribution depends on their interaction. Measuring the diffraction pattern provides information about the crystal-lattice structure. Diffracted waves give rise to peaks that correspond to the distribution of atoms in a material. The provision for diffraction to occur is given by Bragg's law

$$2d \sin\theta = n\lambda \quad (2.33)$$

where d is the interplanar distance for a given set of lattice planes, θ is the incident angle, λ is the wavelength of the X-ray, and n is an integer representing the order of the diffraction peak. This concept is illustrated in Figure 16. XRD measurements can yield useful information regarding II-VI semiconductors, such as crystalline phases, orientations, lattice parameters, strain, and grain size and thickness.

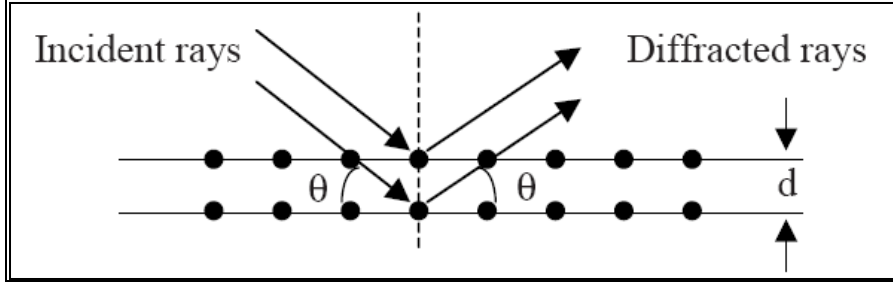


Figure 16. Schematic of diffraction of X-rays by a crystal.⁶⁴

2.11 Scanning Electron Microscopy

For structural characterization via SEM, electrons are emitted from a tungsten cathode and are focused into a narrow beam. The electron beam is deflected over a rectangular area of the specimen surface and transfers energy inelastically to the atomic electrons and to the lattice of the specimen, leading to scattering processes in which some electrons escape to the surface of the specimen. The escaped electrons are collected by a detector and amplified for the output signal. A photomultiplier tube is used to amplify the signal, and the output serves to modulate the intensity of a cathode ray tube. This characterization method is useful for determining surface topography and composition.

2.12 Spectral Ellipsometry

Ellipsometry is an optical technique that measures the output polarization of an elliptically polarized light when a linearly polarized light with known polarization is reflected or transmitted from a sample as shown in Figure 17. The change in this polarization is given as

$$\rho = \tan(\Psi)e^{i\Delta} \quad (2.34)$$

where Ψ is the amplitude ratio and Δ is the phase difference.

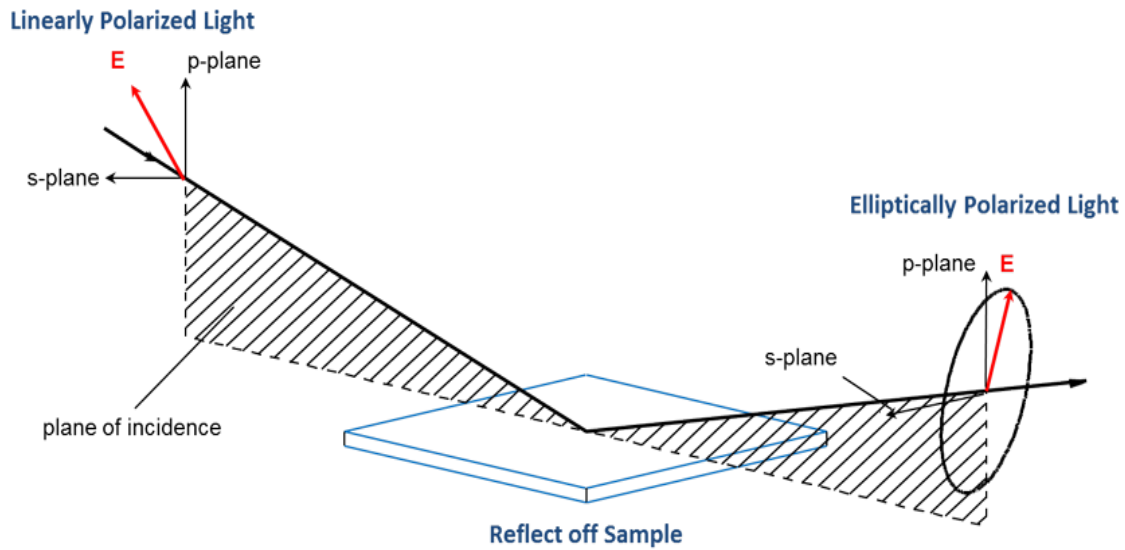


Figure 17. Spectral ellipsometry measurement showing the incident light that is linear with both p- and s- components and the reflected light whose p- and s- polarized light has gone through amplitude and phase changes.⁷⁵

This measured response is determined by the optical properties and the thickness of the sample. Ellipsometry can also be used to obtain information about composition, roughness, crystallinity, and other optical-related material properties.

Ellipsometry measurements for this study were performed with a variable angle spectroscopic ellipsometry (VASE) from J.A. Woollam Co., Inc. The measured data—amplitude ratio, Ψ , and phase difference, Δ —was analyzed by generating a model that closely matches the measured data as presented in the analysis procedure flowchart in Figure 18. Regression analysis was used to find the best match between the experimental data and the model data. Mean square error was used to determine the magnitude of the difference between model data and experimental data. Material properties were then extracted from this analysis.

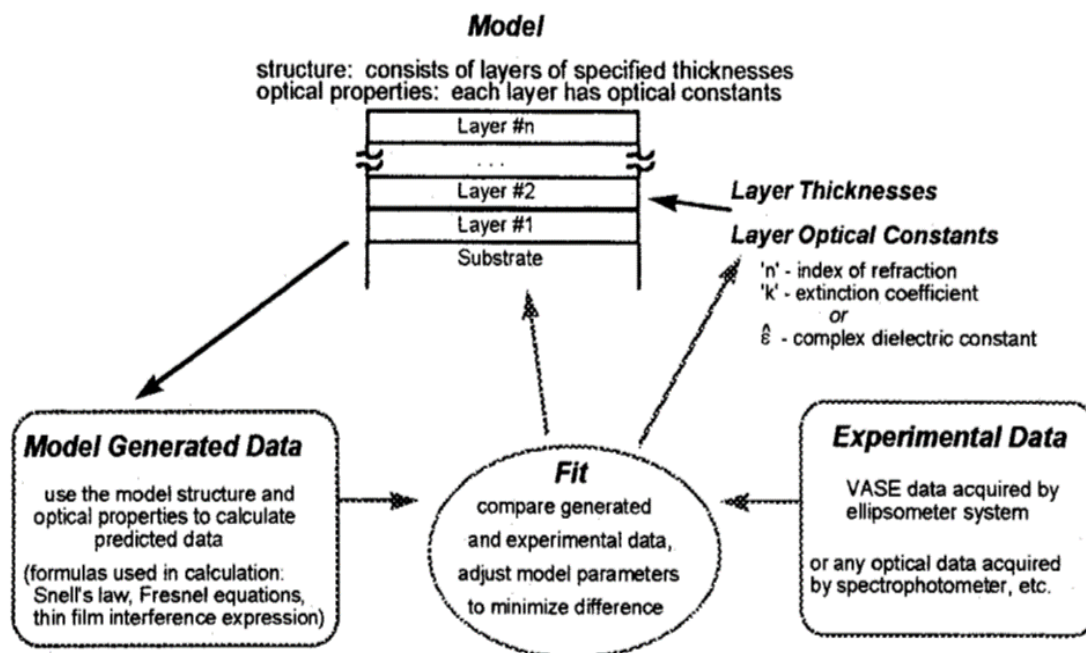


Figure 18. Flowchart of VASE data analysis procedure.⁷⁵

2.13 Atom Probe Tomography

Atom Probe Tomography (APT) is a technique that analyzes a material's chemical composition at the atomic scale and presents the results in a three-dimensional (3D) image. Samples used in APT are prepared in needle shapes. In APT, surface atoms at the apex of needle-shaped samples are removed in succession through field evaporation. Either a high voltage pulse or laser pulse is superposed on a DC voltage supplied to the sample to cause ionization of the surface atoms, which is immediately followed by field evaporation. As shown in Figure 19, ions evaporated from this process are accelerated toward the position sensitive detector (PSD). The exact moment that the ion leaves the sample surface may be referred to as "start time" while the moment the ion reaches the detector may be referred to as "stop time." The information extrapolated from the "start time" and "stop time" is useful for determining time of flight, hence the

chemical nature of each atom. The relationship between total voltage applied ($V_{specimen}$) during the evaporation of an atom, the real distance (L) traveled by the ion to get to the detection system—referred to as “flight length”—the time of flight (t) of the atom, and the mass over charge ratio is given as ⁷⁶

$$\frac{m}{n} = 2eV_{specimen} \times \frac{t^2}{L^2} \quad (2.35)$$

The flight length is deduced from the relative XY position of the atom and the physical distance between the sample and the detector. The known location of an atom on the surface and the time of flight of this atom is used to identify the atom.

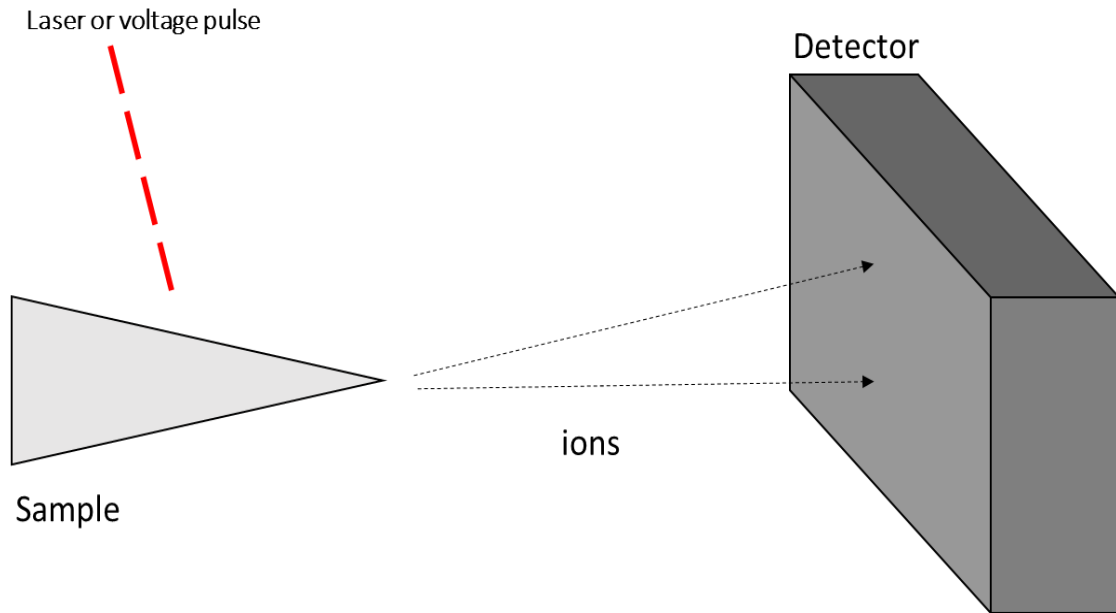


Figure 19. Schematic diagram showing the principles of APT with the detector.

APT measurements for this project were carried out at the Colorado School of Mines with the aid of a laser-pulsed APT to make atomic, spatial, and chemical

resolution measurements in order to analyze the location, uniformity, and concentration of impurity species in CdTe crystal.

2.14 Annealing Station

The annealing station used in this research consisted of a programmable, three-zone tube furnace that can heat up to 1100 °C with a vacuum seal station as shown in Figure 20. Temperature measurements for each zone of the tube furnace were taken using a type K thermocouple to determine the real temperature. A vacuum seal station was set up to vacuum seal quartz ampoules before they were loaded into the furnace for temperature annealing. The vacuum system consists of a turbo-mechanical pump, liquid nitrogen trap, and nitrogen line. Quartz ampoules containing samples are loaded to the vacuum system through the ampoule adaptor and are sealed in vacuum-tight conditions with the use of a welding torch.

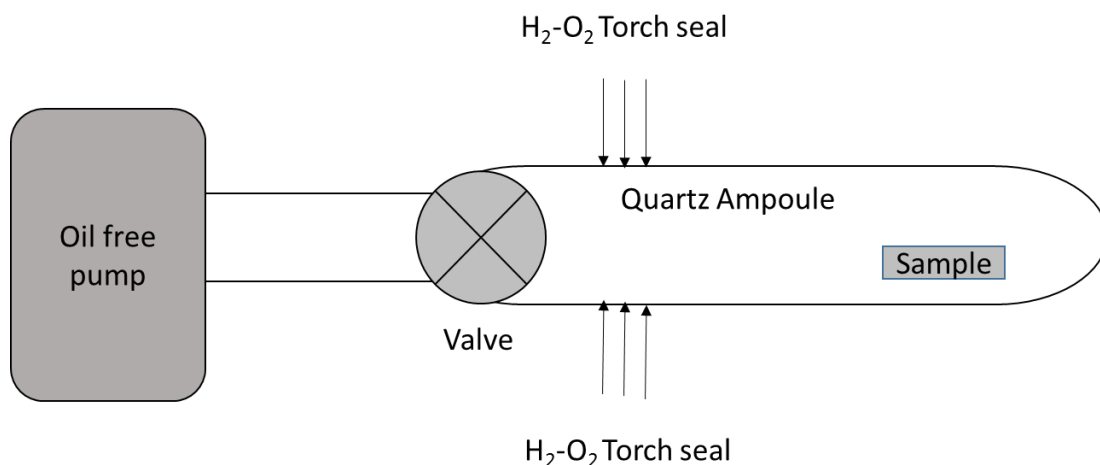


Figure 20. Ampoule seal station setup at Texas State University.

The vacuum system is designed to achieve a pressure of about 5×10^{-6} Torr. Dry nitrogen was incorporated to allow the system to return to atmospheric pressure without becoming contaminated. The vacuum system ensures that the samples are free from

contamination before the annealing process, leading to optimum results in annealing studies. The two annealing studies for this project were dopant activation annealing studies and diffusion annealing studies.

3. MBE GROWTH OF CdTe AND CdTe ALLOYS FOR PHOTOVOLTAIC APPLICATION

3.1 Introduction

CdTe-based solar cells have improved tremendously in device performance in recent years. Efficiency records for polycrystalline CdTe solar cells are frequently broken, recently reaching 21% in 2014.⁷⁷ Yet, there are significant opportunities for improvement of this power conversion efficiency since the current value record remains at more than ten absolute percent below the predicted Shockley–Queisser limit. Power conversion efficiency (η) in solar cells is defined as the ratio of maximum power (P_{max}) compared to the input power (P_{in}) of the solar cell. This efficiency is given as

$$\eta = \frac{P_{max}}{P_{in}} \quad (3.1)$$

The quality of the solar cell is measured by a term called fill factor (FF), which can be derived from the current-voltage (I-V) relationship of a typical solar cell as shown in Figure 21. This I-V's characteristics depict short-circuit current (I_{sc}), open-circuit voltage (V_{oc}), P_{max} , current at maximum point (I_{MP}), voltage at maximum (V_{MP}) point, and theoretical power (P_T). I_{sc} is the current when there is no voltage flowing across the cell while V_{oc} is the voltage when there is no current passing through the cell circuit. I_{MP} is the maximum current at P_{max} while V_{MP} is the voltage at P_{max} .

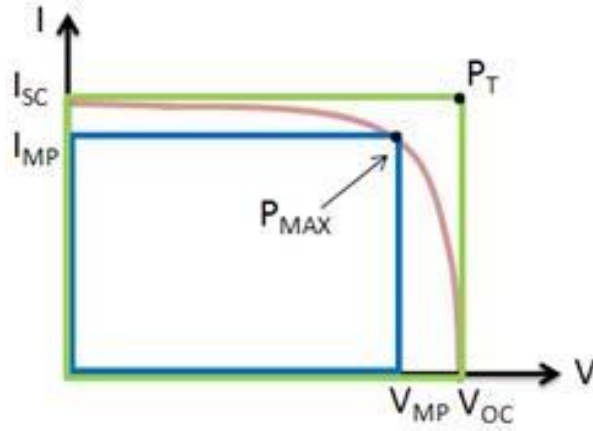


Figure 21. I-V characteristics of a typical solar cell showing the maximum power (P_{max}) and theoretical power (P_T), which are used to determine fill factor (FF).⁷⁸

Fill factor is obtained from the ratio of maximum power (P_{max}) compared to the theoretical power (P_T) obtainable at short-circuit currents (I_{sc}) and open-circuit voltage (V_{oc}) as given below

$$FF = \frac{P_{max}}{P_T} = \frac{P_{max}}{I_{sc}V_{oc}} \quad (3.2)$$

From equation 3.2, an expression for P_{max} can be derived as given below

$$P_{max} = I_{sc}V_{oc}FF \quad (3.3)$$

This expression for P_{max} can be substituted in equation 3.1 as given below

$$\eta = \frac{I_{sc}V_{oc}FF}{P_{in}} \quad (3.4)$$

Studies suggest that short-circuit current density (J_{sc}) is already close to the theoretical limit and that V_{oc} is the primary factor for why current power conversion efficiency is far below the predicted Shockley–Queisser power conversion efficiency limit. Improving V_{oc} becomes important to improving this efficiency. One basic strategy to raise V_{oc} is to improve the built-in voltage by increasing doping in the absorber layer,

but this strategy can lead to reduction in FF when doping exceeds a certain limit thereby affecting overall performance.⁵⁵ The other strategy to improve V_{oc} is through band-gap engineering, which leads to formation of heterostructures that provide carrier confinement in the absorber layer.

The band-gap energy of the material system used to confine the carriers to the photovoltaic absorber must have a band-gap energy that is higher than that of the material used for the photovoltaic absorber. The difference in the band-gap energies of these constituent material systems forming the heterostructure serve as a barrier that blocks thermally excited high-energy carriers. This band-engineered layer can be referred to as an electron reflector if it is designed for limiting electrons.

An electron reflector is a conduction-band energy barrier at the back surface of the solar cell that can reduce the recombination due to the electron flow to the back surface. This is an effective strategy to reduce voltage-limiting recombination at the back surface of the solar cell. A modest back reflector with 0.2 eV will lead to a significant increase of about 25% in the open-circuit voltage even with carrier lifetime as low as 10 ns as shown in Figure 22.⁷⁹

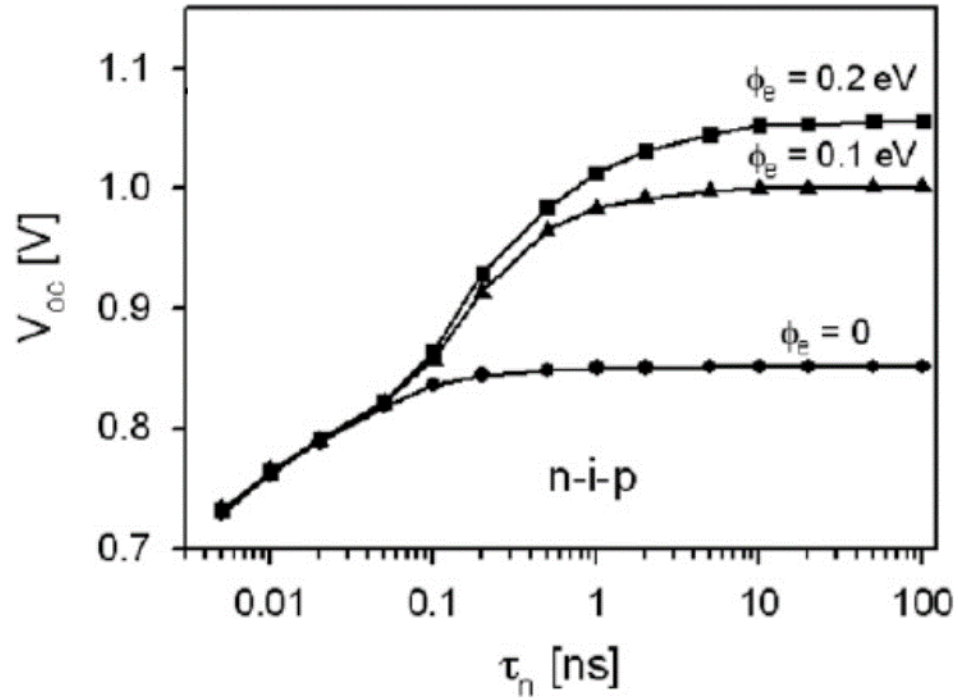


Figure 22. Voltage dependence on lifetime and back-electron barrier.⁷⁹

The major considerations for choosing the barrier layer for the absorber layer are⁸⁰

1. The lattice constant of the barrier layer must be similar to the lattice constant of the absorber layer.
2. The band-gap energy of the barrier layer must be different from the band-gap energy of the absorber layer.
3. Band alignment and offsets

Alloys with Zn and Mg are potential candidates. MgTe and CdTe appear to be the most reasonable alloy combination to form a barrier for CdTe. Figure 23 shows the relationship between band-gap energy and the lattice constant for some semiconductor elements and compounds.

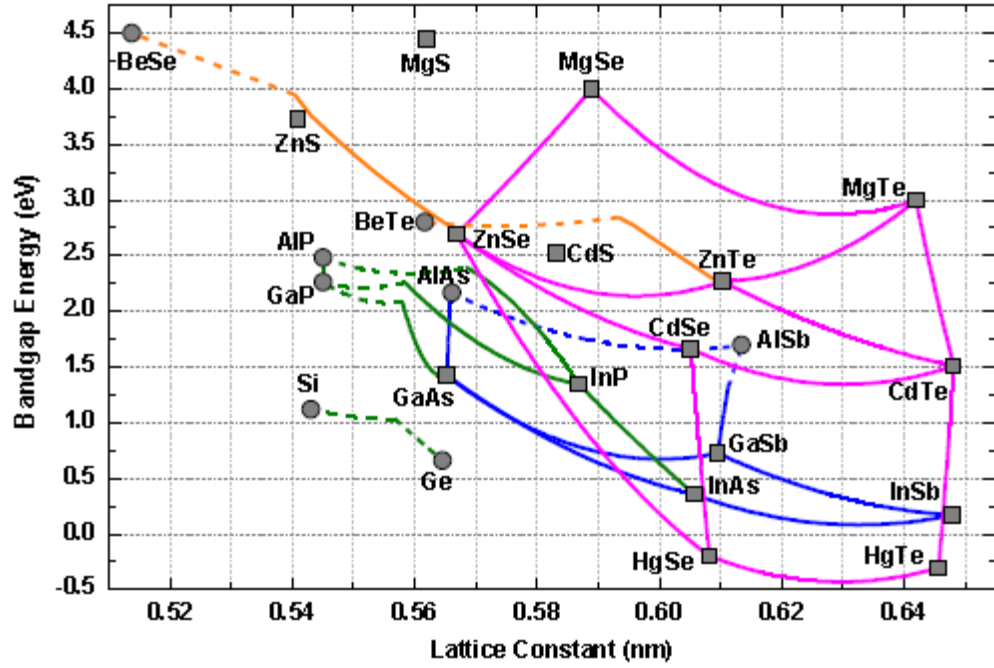


Figure 23. A diagram of experimentally measured band gaps vs. lattice constants of common semiconductors. Solid and dashed lines represent direct and indirect band-gap alloys, respectively.⁸⁰

MgTe has the closest lattice constant and a reasonable, higher band gap compared with CdTe among these candidates. ZnTe has a lower band-gap energy and a much smaller lattice constant than MgTe when considered for CdTe-based barrier layers. As shown in Figure 24, CdTe/CdMgTe heterojunction forms type-I heterojunction, which will reflect both electrons and holes, while a CdTe/CdZnTe heterojunction is predicted to form type-II heterojunction, which would reflect electrons while assisting in hole transport.⁸¹

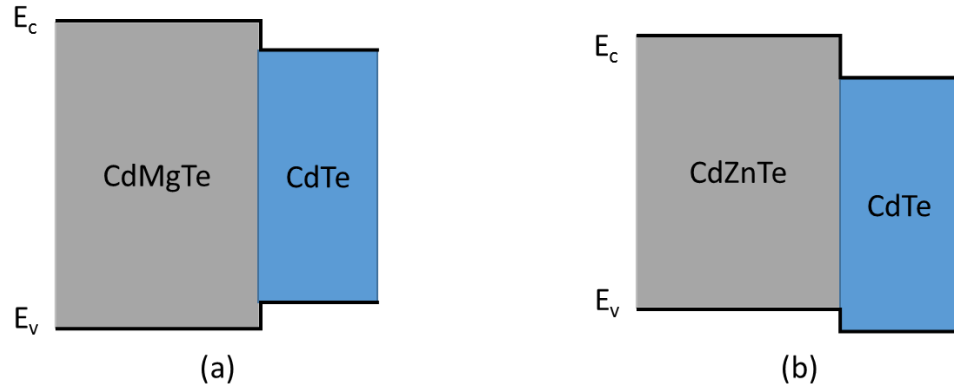


Figure 24. Band alignment of CdTe/CdMgTe (Type I) and CdTe/CdZnTe (Type II) heterojunctions.

The lattice mismatch between MgTe and CdTe was found to be as small as 1.0%^{,31} whereas the lattice mismatch between ZnTe and CdTe is approximately 5.8%, making the CdTe/CdZnTe interface more susceptible to strain-induced electronic defect states, hence, making it have more surface recombination velocity than the CdTe/CdMgTe interface.⁸² Also, CdMgTe provides the largest increase in band gap for the same corresponding change in composition as shown in Figure 25; therefore, CdMgTe was chosen as the barrier material for the design of the structures studied in this research project.

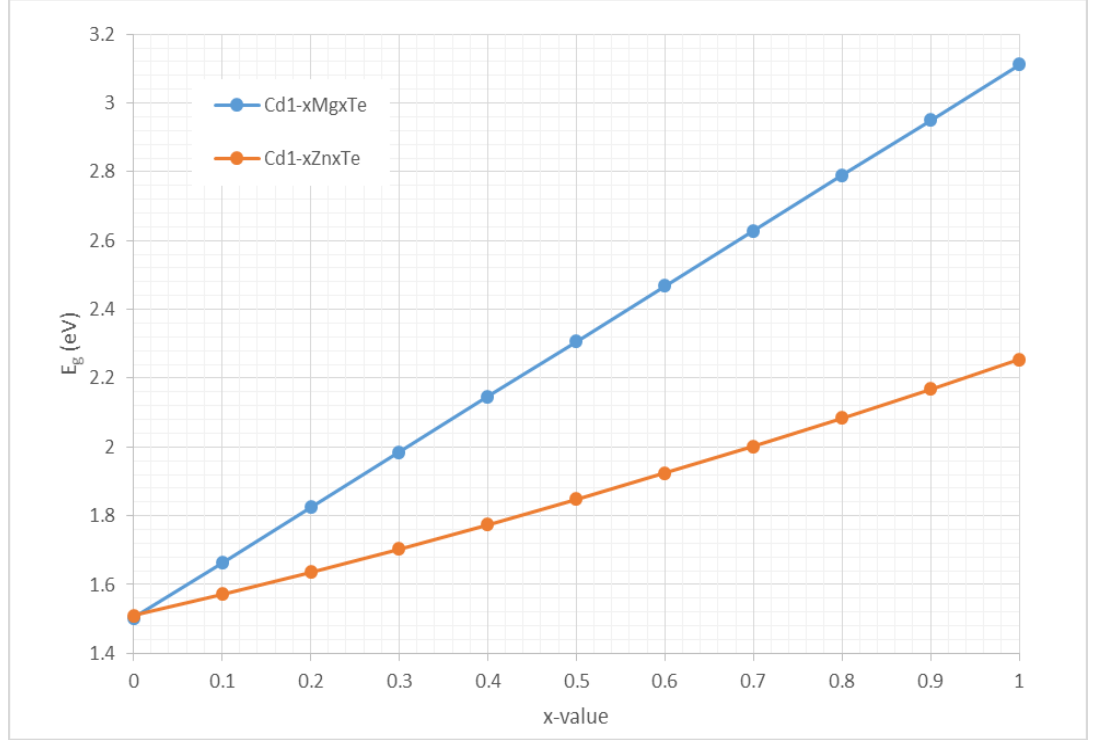


Figure 25. Composition dependence of energy band gap of $\text{Cd}_{1-x}\text{Mg}_x\text{Te}$ ⁸³ and $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$.⁸⁴

To study how doping and band-gap engineering influence solar cell efficiency, different CdTe-based structures were grown via MBE on InSb, CdTe, and CdZnTe substrates with different crystal orientation, primarily (100) and (211) B orientations, while varying growth conditions, such as growth temperature, flux ratios, layer thickness, and layer structure, to optimize CdTe properties for photovoltaic applications. Properties of undoped CdTe were studied to serve as a baseline so that the impact of doping could be better interpreted in the MBE-grown structures.

3.2 Substrate Preparation

One of the most important ingredient for successful MBE growth is the substrate and its surface. The surface of the substrate has direct influence on the arrangement of the adsorbed atoms during MBE growth. Typical as-received substrates usually have surface contaminants, which can later become nucleation sites for defects during growth, hence there is need to prepare the substrate for MBE growth.

3.2.1 InSb substrate

The challenge of achieving structural perfection with commercially available CdTe substrates has prompted the use of other substrates to grow CdTe layers.^{85, 86} One such substrate is InSb. Several research groups have demonstrated MBE growth of high-quality, (100)-oriented CdTe on InSb substrates.⁸⁷⁻⁸⁹ InSb is an attractive substrate choice for the growth of CdTe structures because the lattice mismatch between CdTe and InSb is small at about 0.05%.

Thermal annealing and InSb buffer growth are the two processes used in this project to prepare InSb substrates for the growth of CdTe structures. Wood et al.⁸⁹ show that inclusion of an InSb buffer enhanced the quality of the CdTe layer. Samples grown on epilayer-ready InSb substrates in this project started with InSb buffer layers of about 500 nm grown in the Sb-based chamber at a growth temperature of about 410 °C. After growth, the buffer-deposited substrate was then transferred in-situ to the II-VI chamber via the buffer chambers.

Once in the II-VI chamber, the InSb buffer-deposited substrate was preheated under Sb flux for about ten minutes at an elevated temperature of 620 °C in order to

desorb the oxide that might have bound to the surface during the process of transfer. This thermal annealing yielded a smooth surface that is believed to be characteristic of the stoichiometric condition.⁹⁰ The RHEED reconstructions characteristic of a Sb-stabilized surface—the pseudo-(1×3) pattern—were observed after the heat treatment.

3.2.2 CdTe and CdZnTe substrates

3.2.2.1 *Substrate polishing*

There is need for substrate-surface preparation in II-VI material prior to MBE growth because II-VI substrates are not truly epilayer ready. As-received CdTe substrates usually have a rough surface with polishing damage within 10 μm in depth from the surface resulting in a need for re-polishing to get rid of polishing damage to achieve good crystal growth, thereby improving device performance. As-received substrates were degreased by soaking them in TCE for five minutes at 70 °C, followed by a five-minute soak in acetone at 70 °C, a five-minute soak in methanol at 70 °C, and then another five-minute soak in methanol at 70 °C. This sample-degrease step was followed by either a chemical etching process or a chemo-mechanical polish, which is a chemical etch coupled with either hand polishing or semi-automated polishing.

The initial phase of this study adopted etching as the sole method of preparing sample substrates. Later, the sample preparation process transitioned to hand polishing and, then, to semi-automated polishing (SAP). The etching procedure was carried out by etching as-received substrates in a bromine-methanol (0.5% bromine) solution for five minutes followed by a methanol rinse for about five to ten seconds, then they were dipped in a methanol solution for one minute followed by a methanol rinse for about five

to ten seconds. The methanol dip step was repeated again, and the sample was blow dried and followed by a deionized (DI) water rinse for five minutes where DI water was allowed to flow from the faucet and impinged on the surface as shown in Figure 26. This step was followed by etching the substrate in a hydrochloric acid (HCl)-DI water (10% HCl) solution for five minutes to remove oxide then exposing it to a DI water impingement again for five minutes. The etched sample was then blown dry to complete the etching process.

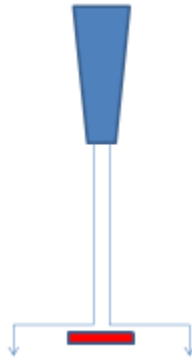


Figure 26. Schematic of how deionized water impinges on sample surface to remove surface contaminants.

In a typical hand-polishing process, as-received substrate is degreased and mounted on a 3-inch diameter, 0.25-inch thick quartz disc with a minimal amount of indium to avoid indium exposure around the outer edges of the substrate. A polishing pad made of poromeric base material is mounted on a 6-inch diameter optical flat disc and then saturated with methanol, which is followed by a 0.5% bromine-methanol solution wet. Then, the surface of the degreased substrate is moved over the polishing pad under the flow of a 0.5% bromine-methanol solution for a specific duration so that uniform surface polishing is achieved. The pad is then quenched with a copious amount of methanol, and the substrate is rinsed with methanol to remove bromine remnants. The

polishing procedure is followed by a five-minute direct flow of DI water to remove any leftover contaminants at the surface. The sample is then blown dry with filtered nitrogen.

The SAP process, unlike the hand-polishing process, involved using a spinner to carry out the polishing task of the etch-and-polish process. Prior to polishing, as-received substrate was degreased by dipping it into trichloroethylene (TCE), acetone, and methanol for ten minutes each at ~85 °C. Degreased substrate was etched by placing it into a dipping basket, then it was dipped into a bromine-methanol (0.5% vol) solution for five minutes. The bromine-methanol etched substrate is thoroughly rinsed using the squirt bottle then dipped into methanol for two minutes to complete the etching step. To begin the polishing step, the spin speed of the spinner is set to 100 rpm while its acceleration is set to 20 rpm, and methanol is used to wet the polishing pad. Using the spinner to spin the substrates under the flow etchants, substrates underwent a brief chemi-mechanical polish with a 250 ml methanol for one minute, a bromine-methanol solution (0.02% vol) for two minutes, and a 500 ml methanol for one minute. The polished samples were then rinsed in a methanol solution for two minutes followed by a five-minute deionized-water rinse, after which they were blown dry with nitrogen.

3.2.2.2 *Atomic Hydrogen cleaning*

Atomic hydrogen cleaning has been demonstrated to be efficient in removing oxide from the surface of substrates for the growth of II-VI semiconductors.^{91, 92} An atomic hydrogen cleaning procedure followed the chemo-mechanical polish procedure as described in section 3.2.2.1. Prior to the atomic hydrogen cleaning procedure, polished substrates were mounted on a sample holder (either with indium on a molybdenum block

or without indium on a Si wafer using an indium-free mask). Mounted substrates were then placed in the load-lock chamber of the MBE system. The load-lock chamber is baked for about two hours and pumped down with a scroll pump to $\leq 10^{-6}$ Torr before the substrate is transferred to the atomic-hydrogen cleaning chamber. The atomic-hydrogen cleaning chamber is equipped with a molecular hydrogen source and a high-temperature gas cracker. The gas cracker is used to crack molecular hydrogen to atomic hydrogen. Atomic hydrogen cleaning of CdTe and CdZnTe substrates was achieved by exposing substrates to the flow of atomic hydrogen with BEP of about 2×10^{-6} Torr for about thirty minutes at a substrate temperature of ~ 200 °C. The atomic-hydrogen cleaned substrate is then transferred into the molecular beam epitaxy (MBE) growth chamber via an ultrahigh vacuum buffer chamber.

3.3 Growth Process

During the MBE growth process, growth of epitaxial layers occurs through the reaction between constituent atoms arriving at the substrate surface and the heated substrate surface. Many surface processes occur during MBE growth. As shown in Figure 27, some of these surface processes are: (1) adsorption of impinging atoms, (2) surface migration of adsorbed atoms (also known as adatoms), (3) lattice incorporation of atoms, and (4) thermal desorption of species that fail to incorporate into crystal lattice. These processes depend on factors such as the type of atoms, the substrate, and the temperature of the substrate, all of which are ultimately responsible for the growth of thin layers on the substrate and its quality. Hence, just as surface preparation is important, understanding and controlling growth parameters, such as temperature, growth rate, and

Cd overpressure, become vital to growing structures with good material properties successfully.

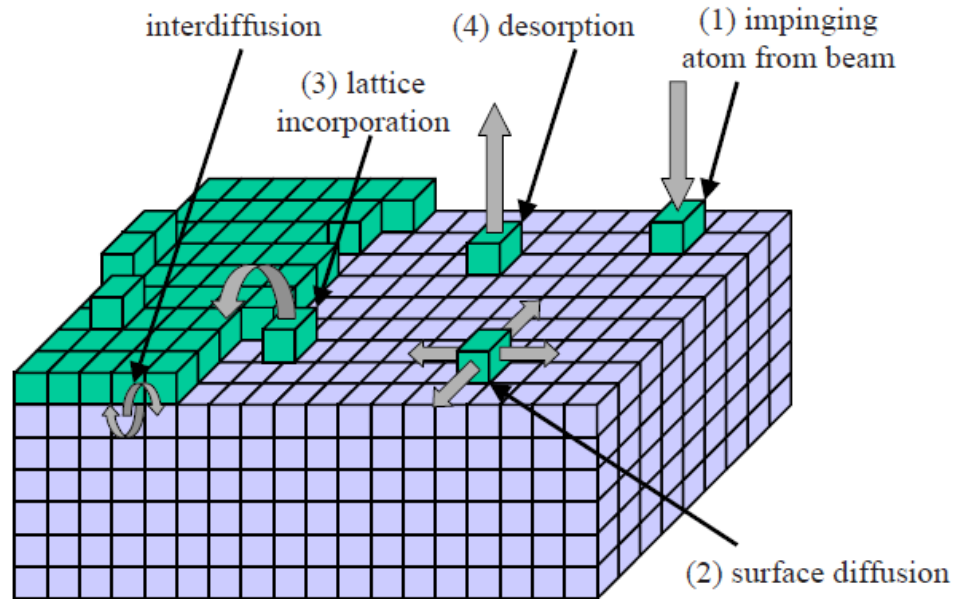


Figure 27. Schematic diagram showing some of the surface processes in MBE epitaxial growth.⁶⁴

3.3.1 Growth rate calibration

Understanding the stoichiometry of the incident beams and substrate temperatures are useful for the control of thickness,⁹³ and defect formation,⁶⁰ in growing CdTe layers. Controlling substrate temperature becomes one of the most important task for the MBE grower.⁹⁴ Substrate temperature has the ability to influence some of the MBE growth process such as the rate at which atoms diffuse at the surface of the substrate and desorb. RHEED technique can be used to probe these surface processes. In this project, RHEED oscillations were used to determine the growth rate of CdTe from MBE growth process. The behavior of the CdTe growth rate as a function of temperature and Cd flux were studied.

For this project, growth rate experiments were performed under similar conditions. By using the same growth conditions, results can be accurately compared over time. To measure the growth rate of CdTe, a layer of at least 500 nm-thick CdTe was first deposited under Cd overpressure condition and fixed substrate growth temperature in order to have a smooth surface before starting the RHEED measurement. After achieving a smooth surface as indicated by a streaky RHEED pattern, the CdTe molecular beam, at a fixed substrate temperature, was interrupted briefly by closing the mechanical shutter for few seconds while the Cd molecular beam was not interrupted. Then, the RHEED oscillation measurement started, and the shutter of the CdTe cell was opened after few seconds of starting the RHEED oscillation measurement. The resulting RHEED intensity measurement, using the specular spot, showed RHEED signal intensity oscillations of the growing layer as a function of time. This signal intensity's oscillations generated over a period of time—usually not more than sixty seconds—typically have more than fifteen periods before damping out as shown in Figure 28. The growth rate in monolayer per second (ML/s) is then determined by simply counting the number of undamped oscillations and averaging the oscillations over time.

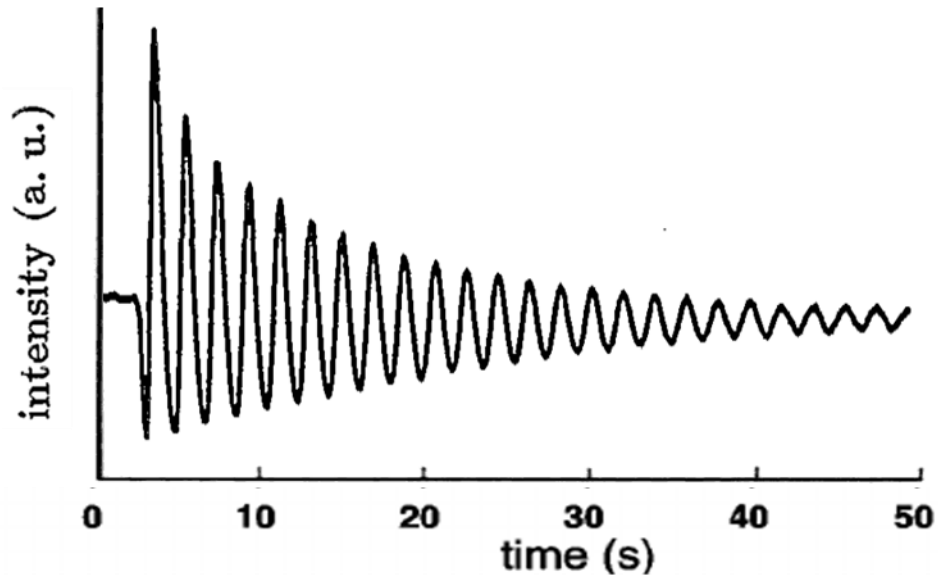


Figure 28. Typical RHEED oscillations for CdTe growth on CdTe (100).

The growth temperature and the fluxes of the constituent material were optimized to generate high-intensity oscillations. RHEED oscillations were then used to measure growth rate as a function of Cd flux as shown in Figure 29. In this experiment, the substrate temperature on InSb (100) substrate was fixed at $\sim 290^\circ\text{C}$, and CdTe flux was fixed at $\sim 6.6 \times 10^{-7}$ Torr while Cd flux was varied as a fraction of the fixed CdTe flux. Cd flux was monitored to ensure minimal fluctuation during the experiment, and growth rate measurements were taken for different Cd fluxes. As shown in Figure 29, the growth rate increased linearly with Cd flux increase up until a Cd/CdTe ratio of 0.2 but becomes nearly fixed for Cd/CdTe flux ratios between 0.2 and 0.3. No RHEED oscillations were observed when the Cd/CdTe flux ratio was increased to ~ 0.4 . The point where the dependence of growth rate on Cd flux changes from a near-linear-dependent relationship to a near-independent relationship, which is indicated in Figure 29, is considered the

stoichiometric point.⁹⁵ This point, which occurs around ~ 0.2 Cd/CdTe flux ratio in this experiment, characterizes the transition from the (2x1) Te-rich to the c(2x2) Cd-rich surface.

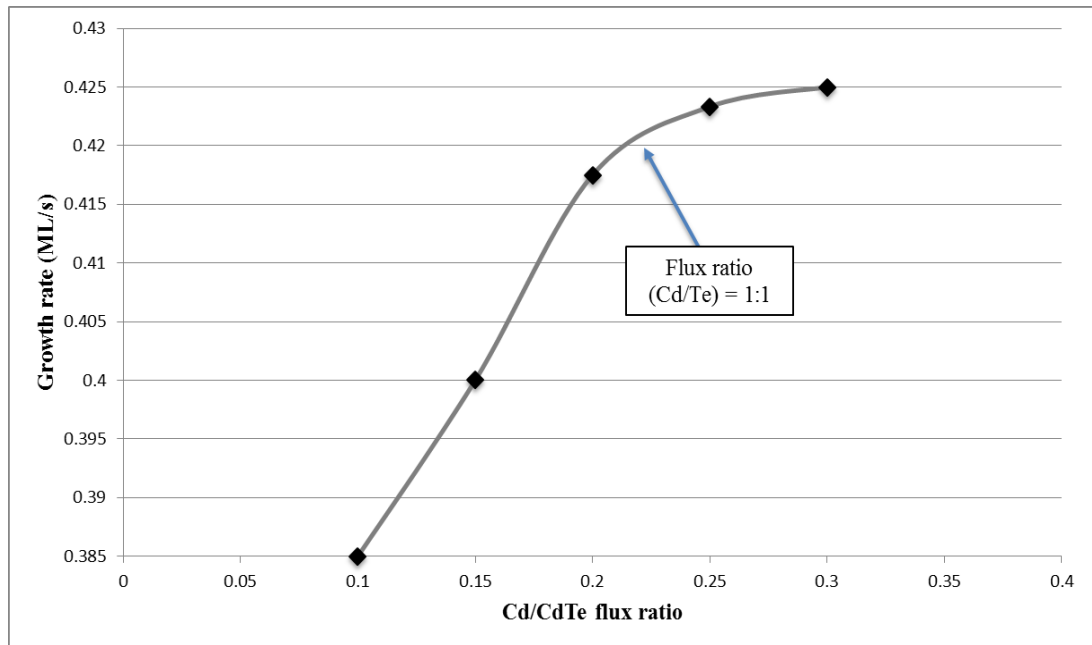


Figure 29. CdTe growth rate as a function of Cd flux at ~ 290 °C substrate temperature.

Also, growth rate was determined at various substrate temperatures in order to derive the temperature window for CdTe growth processes as shown in Figure 30. These measurements were performed on a regular basis over a period of time using CdTe (100) and InSb (100) substrates. During a typical growth rate versus temperature, CdTe was fixed at $\sim 6 \times 10^{-7}$ Torr and the Cd/CdTe ratio at ~ 0.2 , while the temperature was varied.

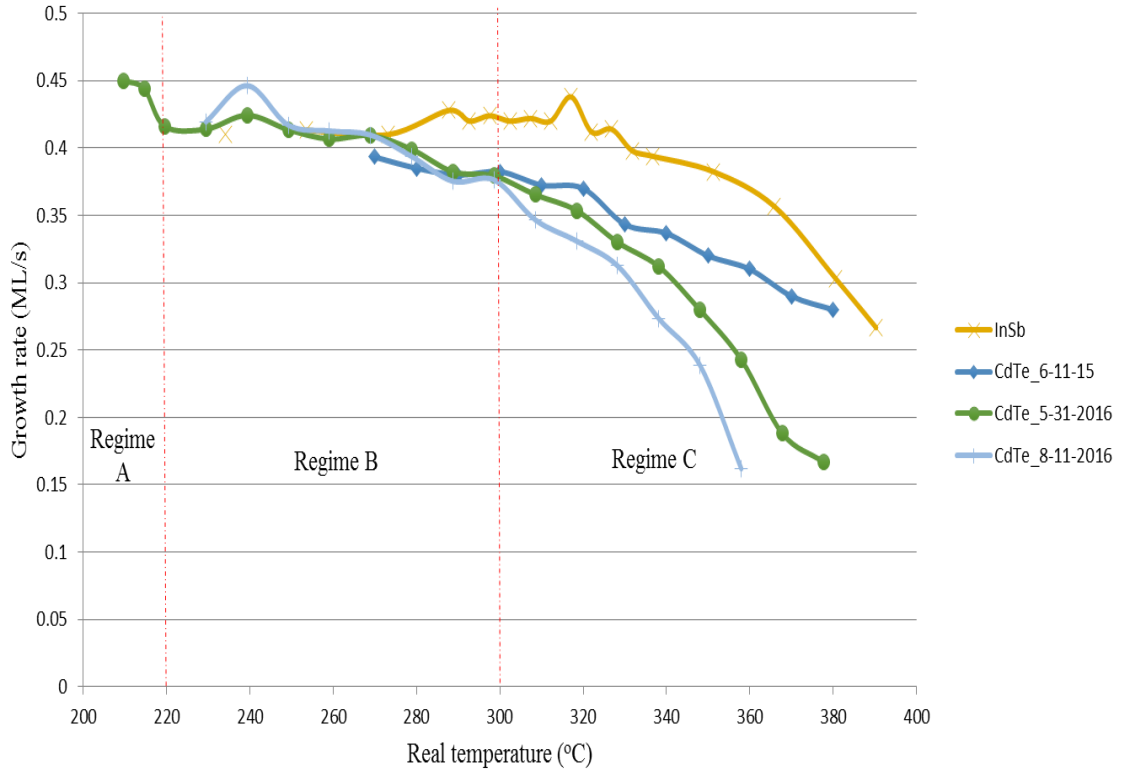


Figure 30. Growth rate vs. temperature of CdTe growth on InSb (100) and CdTe (100) substrates.

Three regimes were observed in all the growth rate experiments performed. These regimes are labelled A, B, and C in the growth rate-temperature profile as shown in Figure 30. In regime A, the growth rate was limited by surface reaction such as surface roughening and fast nucleation. Typically, no RHEED oscillations were observed in this regime. For regime B, growth rate was limited by diffusion or mass transfer across the boundary. Here, growth rate depended on the flow of the source materials impinging on the substrate surface and the diffusion coefficient of these source materials. In this regime, growth rate was nearly constant over a wide range of temperature, which is considered the growth temperature window. This is mostly the desired regime for good

quality growth because there is control of growth rate and temperature sensitivity is minimized. For regime C, growth rate was limited by crystal decomposition. In this regime, desorption is approximately the same as deposition, hence no growth occurs.

The growth temperature window from regime B was used to guide the substrate temperature choice throughout this project. When growth temperatures fall in regime A, growth layers will lose their crystallinity, and for growth temperatures that fall within regime C, almost all the deposited atoms will desorb and growth will not occur. Also, point defect formation was enhanced. In this study, for CdTe with Cd overpressure, the observed growth temperature window for regime B was from ~ 220 °C to ~ 300 °C, and the growth rate for the growth temperature window was ~ 0.4 ML/s. The observations made in this project were comparable with studies of other research groups.^{60, 93, 96}

Prior to each growth rate experiment, temperature calibration experiments were performed. Temperature calibrations were used to measure and account for substrate temperature drift, which is a major problem with MBE since the thermocouple that is meant to monitor the substrate temperature is usually not in thermal contact with the substrate holder because of the substrate rotation requirement needed for compositional uniformity of grown layers.⁹⁷ Temperature calibrations were carried out regularly to ensure that experiments were properly controlled. Techniques, such as In melting, InSb melting, Pb melting, and RHEED oscillations with high and low cut-off points, were used for temperature-calibration experiments.

For indium-melting experiments, small pieces of indium were mounted on samples, and indium melting was visually inspected as the II-VI MBE system dial temperature gradually increased. The dial temperature at which the indium piece melted

visually was recorded, and the difference between this visually inspected melting point and the actual melting point of indium, which is 156 °C, was determined to be the primary deviation from the actual temperature. The temperature difference was then applied to subsequent dial temperatures to determine the “real” substrate temperatures. In addition to this indium-melting experiment, InSb melting was determined with the same visual method used for the indium-melting experiment, and the visually inspected melting point was compared to the actual melting point of InSb, which is 525 °C. These temperature calibrations were used to determine “real” temperatures for RHEED oscillation cut-off points for CdTe film grown on InSb (100) that was mounted on a molybdenum block. These cut-off points refer to the temperatures where there is no longer RHEED oscillations during RHEED-oscillation measurements at varying temperatures. The lower temperature limit (T_L) refers to a low temperature cut-off point, while the upper temperature limit (T_H) refers to the high cut-off point of the RHEED oscillations. From these calibrations, “real” T_L and T_H were determined to be 229 °C and 395 °C, respectively.

Temperature calibrations were also performed for CdTe film grown on CdTe (100) that was mounted with an In-free mask. Substrate dial temperatures for In-melting, Pb-melting, T_L , and T_H were compared to “real” temperatures as presented in Table 7. As shown in Figure 31, a linear relationship is observed between substrate dial temperature and the “real” substrate temperature.

Table 7. Comparison of real temperature to substrate dial temperature for CdTe film grown on CdTe (100) that was mounted with an In-free mask.

Method	Real temperature (°C)	Substrate dial temperature (°C)
In melting	156	228
Pb melting	327.5	422
RHEED T_L	229	287
RHEED T_H	395	455

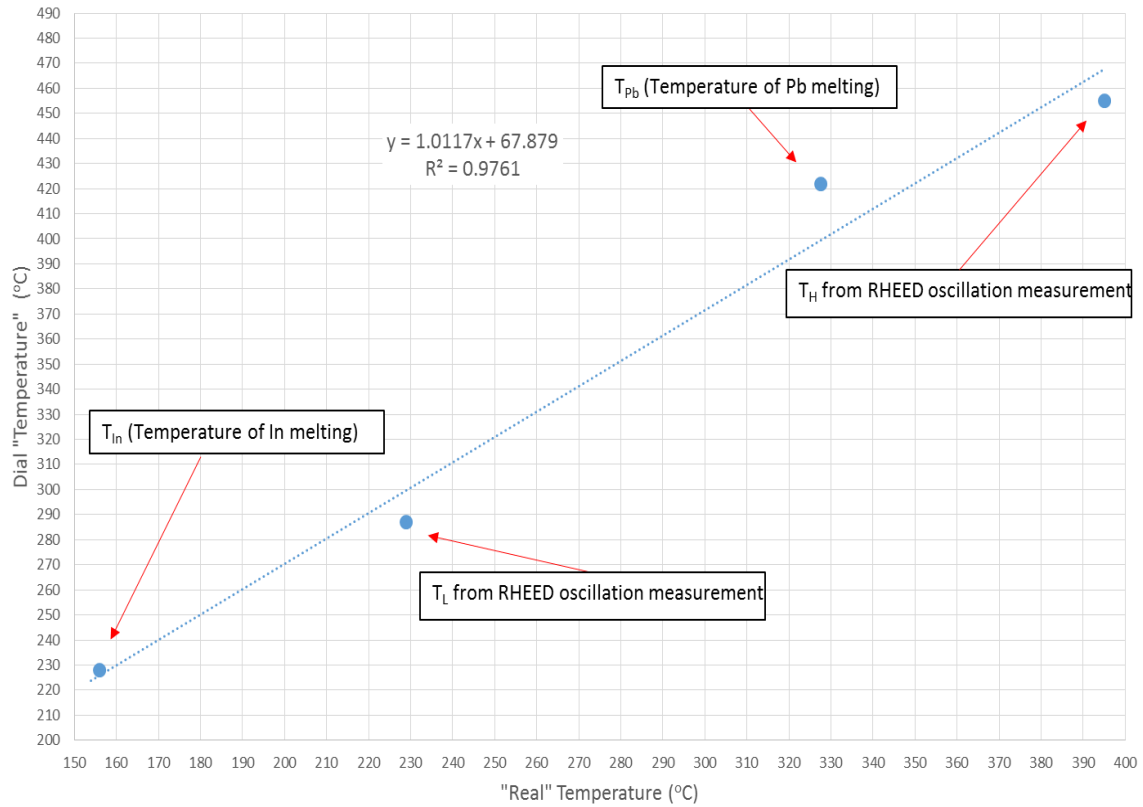


Figure 31. Real temperature vs Substrate dial temperature.

The linear equation derived from the relationship between the real temperature and measured dial temperature is given as

$$y = 1.0117x + 67.879 \quad (3.5)$$

Where y is the dial temperature and x is real temperature in degrees Celsius. To have an expression for the real temperature, the linear equation can be rearranged as

$$x = \frac{y-67.879}{1.0117} \quad (3.6)$$

3.3.2 Migration enhanced epitaxy

Migration enhanced epitaxy (MEE) is a pulse technique consisting of supplying reactant species to the substrate surface in order to smoothen it before growth. In MEE growth, constituent elements are timed and alternated for a specific number of deposition cycle. In MEE growth for this project, the Cd shutter was opened so that the substrate surface was exposed to Cd flux for sixty seconds in order to produce a Cd-stable surface. After this sixty seconds, the CdTe shutter is opened for three seconds for CdTe exposure and closed for sixty seconds before it opens again while the Cd shutter is left open for constant Cd exposure all through the MEE process. The opening of the CdTe shutter and the expiration of the sixty seconds of dead time before the next CdTe exposure is considered a complete cycle. Typically, the MEE process consist of many cycles of CdTe exposure, and it is performed with regular growth conditions. MEE growth experiments results studied with AFM suggest that ~20 to 50 cycles is sufficient to have a smooth starting surface for CdTe MBE growth. The typical MEE layer is ~10 to 20 nm thick.

InSb substrates and atomic-hydrogen cleaned CdTe and CdZnTe substrates were preheated at temperatures above the growth temperature in order to desorb oxide that might be present at the surface prior to this MEE growth. Epitaxial-layer growth followed this MEE growth.

3.3.3 MBE growth of CdTe

During MBE growth, atoms are adsorbed onto the surface of the substrate where they can locate a nucleation center, form a nucleation center, or desorb. Information from RHEED in the form of surface reconstruction, which provides information about adsorption and desorption activities, is useful for making decisions about adjusting growth conditions to achieve structures of good quality.

MBE growth of CdTe (100) under stoichiometric conditions results in a (2x1) surface reconstruction. Under this condition, it is believed that the surface of the CdTe layer is rich in Te atoms,^{60, 93, 95} which are weakly bound to the surface.⁶⁰ These weakly bound Te atoms can lead to defect formation in growing CdTe layers but can be controlled by the use of Cd overpressure.⁶⁰ Also, the effect of interfacial reaction in the growth of CdTe/InSb heterostructures, which leads to Cd deficiency, may be reduced by overpressure.⁹⁸

Based on the growth rate experiments described in section 3.3.1, the Cd overpressure needed to achieve quality growth is approximately 20% of the CdTe flux. Growth rate for most of the grown structures was maintained at 0.4 ML/s to ensure reproducibility. Based on the observation of growth rate experiments, a range from 240 °C to 270 °C was established as the substrate temperature, which is where optimal growth is achieved. Usually, most growth was planned and performed at 240 °C, but adjustments were made in some cases depending on the feedback from the RHEED pattern.

3.3.4 MBE growth of CdTe alloys

Alloying in this project was used to achieve different purposes. CdMgTe, CdSeTe, and CdZnTe alloys were grown to achieve electron confinement, lattice matching, and As doping, respectively.

CdMgTe is expected to be more effective in confining thermally excited high-energy carriers than CdZnTe, thereby serving as a more effective barrier layer in CdTe.

Schematic diagrams for a CdTe/MgCdTe single heterostructure and double heterostructure are shown in Figures 32 and 33.

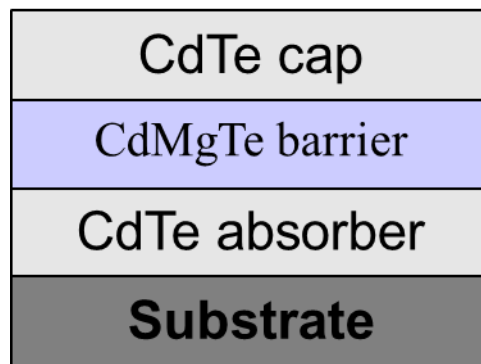


Figure 32. CdTe/MgCdTe single heterostructure.

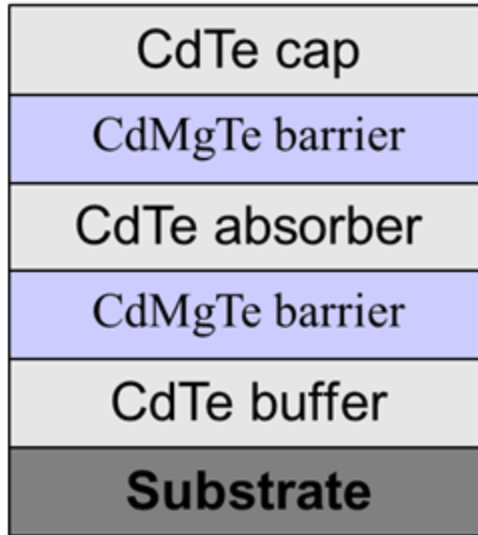


Figure 33. CdTe/MgCdTe double heterostructure.

The barrier layers are expected to prevent the carriers from leaving the absorber layer; however, carriers confined in the single heterostructure can still escape from the bottom side of the absorber layer since this side is not passivated with the CdMgTe layer. The double heterostructure is more effective in confining these carriers since both the top and the bottom side of the absorber layer are passivated with the CdMgTe surface. The CdTe cap layer is used to protect the Mg in the top barrier from oxidation. The band diagram of this CdTe/MgCdTe DH structure is shown in Figure 34 with the recombination mechanisms involved.

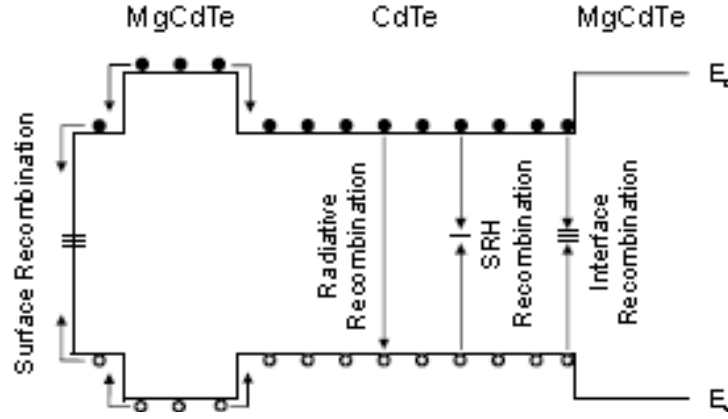


Figure 34. Schematic band-edge diagram for the CdTe/MgCdTe DH structure.⁸⁰

Surface recombination, radiative recombination, Shockley-Read-Hall (SRH) recombination, and interface recombination are all expected to be present in the DHs. The expected lifetime of the carrier in this structure is given as ⁹⁹

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_{rad}} + \frac{1}{\tau_{SRH}} + \frac{2S}{d} \quad (3.7)$$

where τ_{eff} is the effective lifetime, τ_{rad} is the lifetime due to the radiative process, τ_{SRH} is the lifetime due to SRH process, S is the interface recombination velocity, and d is the absorber layer thickness.

The effect of CdTe/CdMgTe lattice mismatch was minimized by carefully designing the Mg composition in CdMgTe. In addition, the thickness of the CdMgTe was carefully designed to ensure that the thickness beyond which misfit dislocations are generated—known as critical layer thickness—was not exceeded for the chosen Mg composition. The thicknesses of the CdMgTe barrier layers was maintained at 30 nm for most of the grown heterostructures based on the critical thickness of the CdTe/ Cd_{1-x}Mg_xTe layer estimated using $x \sim 35\%$, being the optimal x value used in this project. This critical layer thickness was determined using the Matthews and Blakeslee model,¹⁰⁰ and

was estimated to be around 37 nm for the CdTe/Cd_{0.65}Mg_{0.35}Te layer, which has about 0.34% mismatch. The thicknesses of the buffers and absorbers were varied in order to study the impact of their thicknesses on the properties of the grown structures.

In order to lattice match CdTe with the InSb buffer layer on InSb substrates, a small composition of selenium was used to alloy the CdTe. CdTe structures grown on InSb began with a buffer layer of InSb grown in a dedicated III-Sb MBE chamber, followed by a buffer of CdSe_xTe_{1-x}, which had a small composition of $x \sim 1\%$ selenium in order to assume a full lattice match with the InSb.⁶⁸ For the purpose of Arsenic doping enhancement in CdTe, the Zn composition of about 4% in Cd_{1-x}Zn_xTe was used to alloy CdTe. These Cd_{1-x}Zn_xTe structures were grown on Cd_{1-x}Zn_xTe substrates.

3.4 Post-Growth Characterization

After MBE growth, grown CdTe based structures were characterized by various techniques. The results were analyzed for gaining understanding useful in improving the efficiency of CdTe-based photovoltaics while adding to the general knowledge of CdTe for other applications. The structural quality of grown structures was analyzed with cPL to analyze their defect densities. AFM was used as a quick and additional analytical technique to test structural quality, mainly providing information about the surface roughness.

3.4.1 Structural characterization – cPL and AFM

3.4.1.1 Substrate preparation study

3.4.1.1.1 InSb substrates

CdTe-based layers grown on (100)-oriented InSb were studied using confocal PL. Twin-related defects were observed in these CdTe layers. The density of these twin-related defects range from low 10^4 cm^{-2} to high 10^6 cm^{-2} , and the background dislocation defect is usually not more than $\sim 10^5 \text{ cm}^{-2}$. Typical confocal PL results for CdTe layers grown on an InSb substrate are shown in Figure 35. CdTe layers grown on an InSb substrate can show relaxation when the CdTe layer thickness exceeds the critical layer thickness ($\sim 2.95 \mu\text{m}$ for CdTe layers grown on an (100)-oriented InSb)¹⁰¹ due to the lattice-match imperfection between CdTe and InSb.

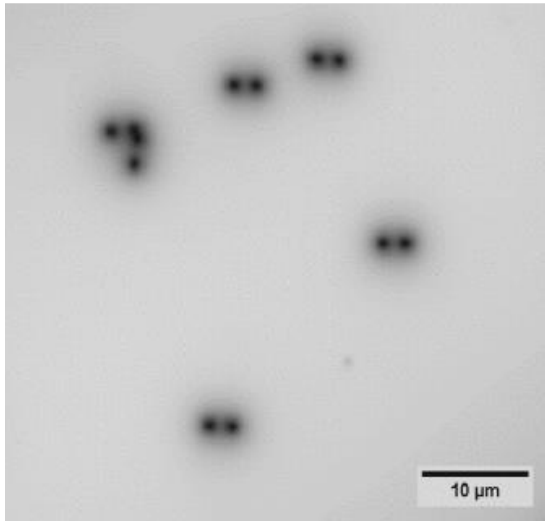


Figure 35. Confocal PL micrograph of a 2 μm thick CdTe/CdMgTe DH grown on (100)-oriented InSb substrate.

Relaxation was visibly noticed in a c-PL image of a CdTe/CdMgTe double heterostructure with a total thickness of 3 μm and a defect density $\sim 1 \times 10^6 \text{ cm}^{-2}$ as shown in Figure 36 where the dark-line defects represent misfit dislocations, and the dark-spots

defects represent twin-related defects. Generally, misfit dislocations were observed in all CdTe layers grown above the critical layer thickness.

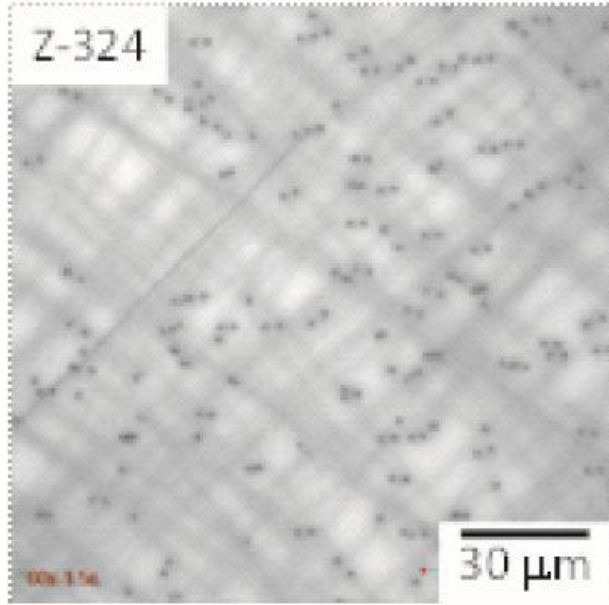


Figure 36. Confocal PL micrograph of a 3 μm thick CdTe/CdMgTe DH grown on (100)-oriented InSb substrate.

Since CdTe and InSb are not perfectly lattice-matched, Se composition of $\sim 1\%$ in CdTe_{1-x}Se_x alloy was used to achieve a lattice-match condition in growing quality epitaxial CdTe layers, especially in layers where the total thickness exceed 2 μm . A typical Se-alloyed CdTe grown in the double heterostructure configuration with 5 μm absorbing layer, shown in figure 37, had a low overall defect density averaging $1 \times 10^4 \text{ cm}^{-2}$ and did not show evidence of relaxation.

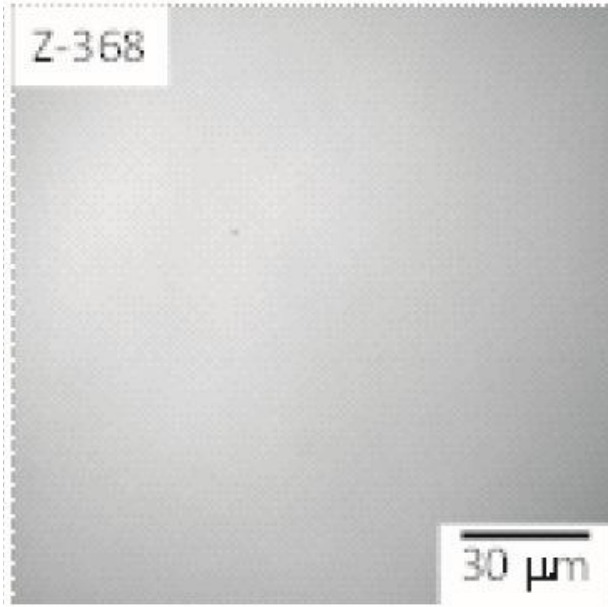


Figure 37. Confocal PL micrograph of a 6.5 μm CdSeTe/CdMgTe double heterostructure grown on (100)-oriented InSb substrate.

3.4.1.1.2 CdTe substrates

As-received CdTe samples usually have rough surfaces due to polishing damage within 10 μm depth from the surface, hence the need for re-polishing to get rid of this polishing damage in order to be able to achieve good crystal growth ultimately improving device performance. The effects of the polishing procedure outlined in section 3.2.2.1 were studied. Epilayers grown on substrates that were not polished but simply etched per vendors' procedure show a defect density at around mid- 10^7 cm^{-2} or larger.

Surface preparation techniques, such as atomic-hydrogen cleaning, MEE, and brief flux exposure before growth, were applied to some of these samples, but these techniques were not enough to keep the defect density below 10^7 cm^{-2} . The effect of migration-enhanced epitaxy (MEE) was studied in these samples. MEE was applied to passivate the surface of z-218 and z-228, but it was not applied to z-219 and z-226. As

shown in Figure 38, the cPL imaging of the defect density suggests that migration-enhanced epitaxy helps growth initiation, but it is not enough to keep the defect density below 10^7 cm^{-2} . The effect of substrate polishing on defect density was also studied.

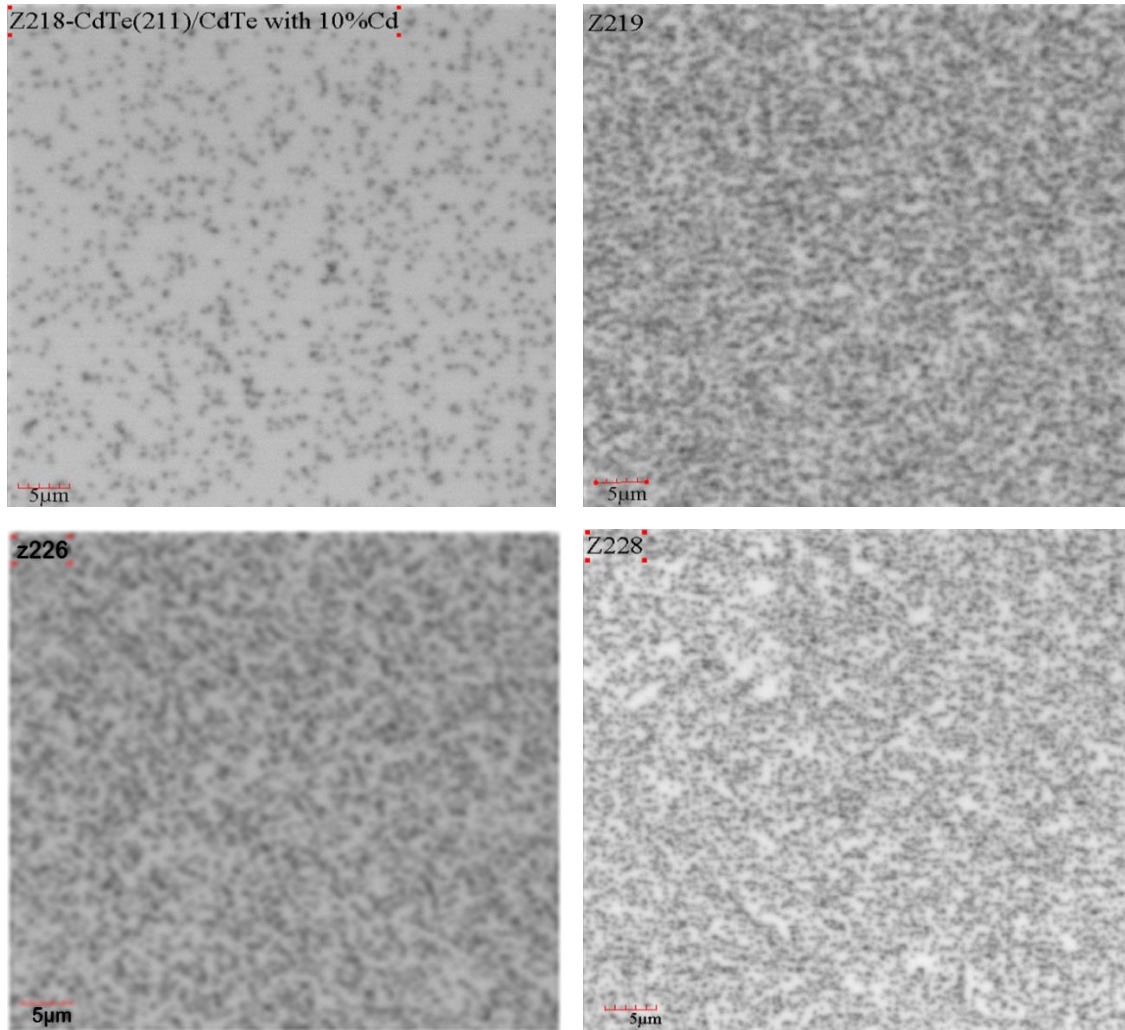


Figure 38. cPL images showing defect density $> 3 \times 10^7 \text{ cm}^{-2}$. Samples were etched in a bromine-methanol solution and grown at 300°C . Z-218 was etched with 0.5% br-methanol, exposed to tellurium flux before MEE and grown with 10% Cd overpressure. Z-219 was etched with 0.5% Br-methanol, exposed to tellurium flux before growth with no MEE, and grown with 10% Cd overpressure. Z-226 was etched with 1% Br-methanol, exposed to tellurium flux before growth with no MEE, and grown with 10% Cd overpressure. Z-228 was etched with 1% Br-methanol, exposed to tellurium flux before MEE, and grown with 10% Cd overpressure.

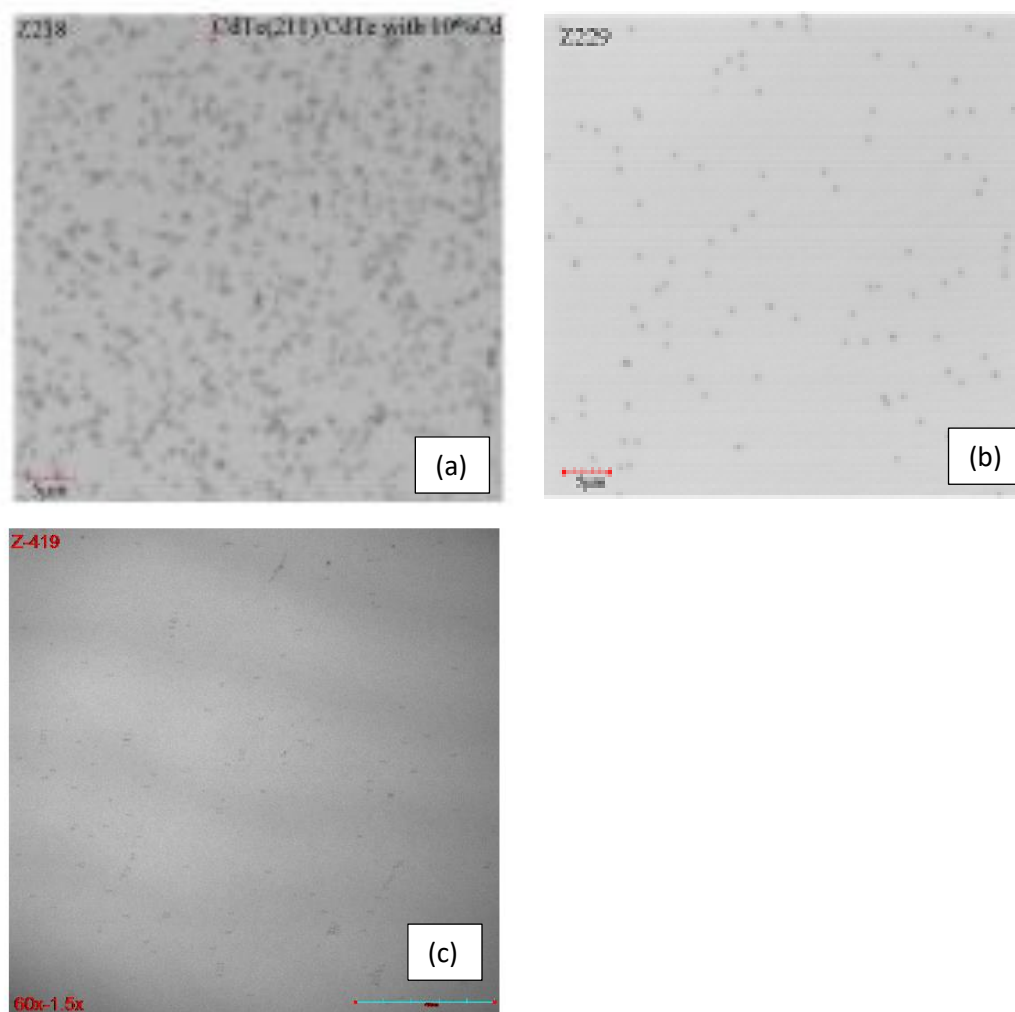


Figure 39. (a) Substrate was etched prior CdTe growth. Defect density $> 1 \times 10^7 \text{ cm}^{-2}$. (b) Substrate was hand-polished prior CdTe growth. Defect density - $1 \times 10^6 \text{ cm}^{-2}$ to $1 \times 10^7 \text{ cm}^{-2}$. (c) Substrate semi-automatically polished prior CdTe growth. Defect density $< 1 \times 10^6 \text{ cm}^{-2}$.

Figure 39 shows a comparison of samples that were grown with identical procedures but differ in substrate-preparation technique: standard Br-methanol etching, hand polishing, and semi-automated polish techniques. The cPL micrograph shows lower defect density with samples grown with hand-polished substrates with one order of magnitude. This polishing process was modified by making the hand-polishing process a

semi-automatic one with the use of a spinner in order to improve the uniformity of the surface polish.

The effect of polishing time was studied in CdTe substrates where substrates were polished for different durations of time. The polishing times that were considered in this study are one minute, two minutes, and three minutes. AFM and cPL images of samples z-240 to z-243 as shown in Figures 40 and 41, respectively, show low surface roughness RMS values for both samples and a higher defect density for z-240 as presented in Table 8, suggesting that a polishing time of two minutes is more effective than a one-minute polish.

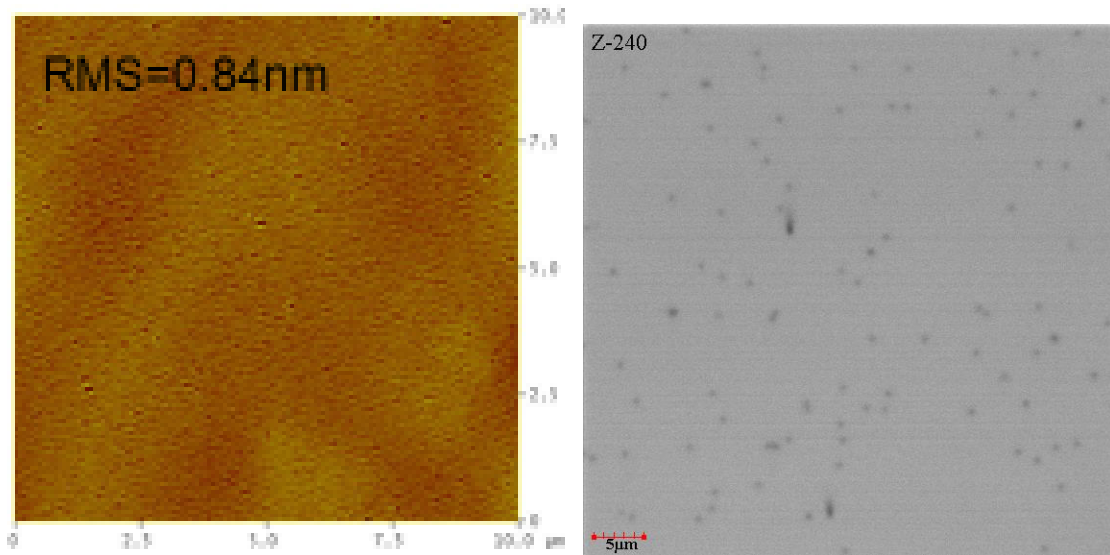


Figure 40. Sample z-240 has $3 \times 10^6 \text{ cm}^{-2}$ defect density. Hand polished for 1 minutes.

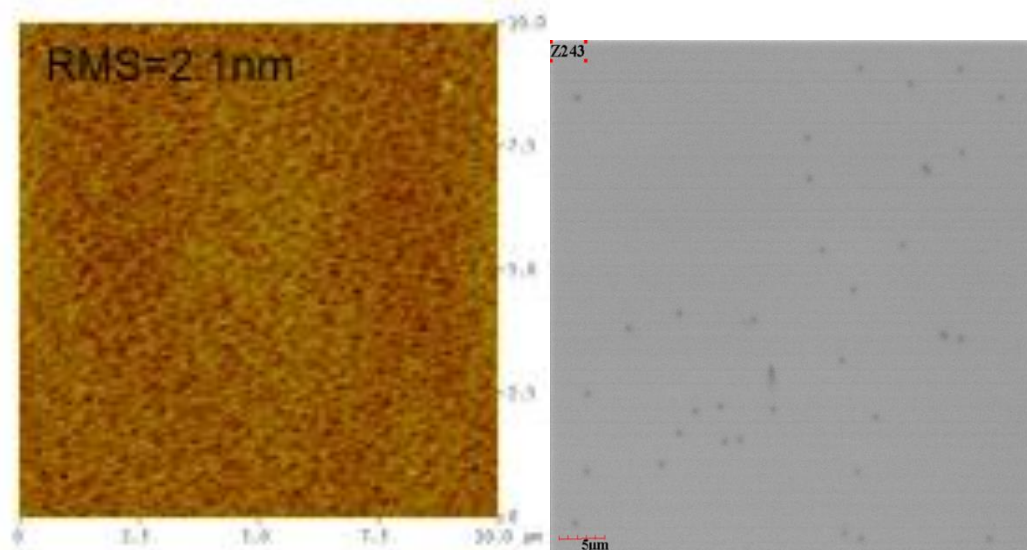


Figure 41. Sample z-243 has $1.5 \times 10^6 \text{ cm}^{-2}$ defect density. Hand-polished for two minutes.

Table 8. Comparison of polishing time, RMS values, and defect densities in samples that were polished prior to CdTe growth.

Sample number	Polishing time	RMS value determined by AFM (nm)	Defect density determined by cPL (/cm ²)
Z240	1 minute	0.84	3E6
Z243	2 minute	2.1	1.5E6

An improved polishing technique for the CdTe substrate surface reduced the dislocation content to the mid- 10^5 cm^{-2} as shown in Figure 42, and defect density below 10^6 cm^{-2} was reproducibly achieved in most CdTe and CdZnTe substrates

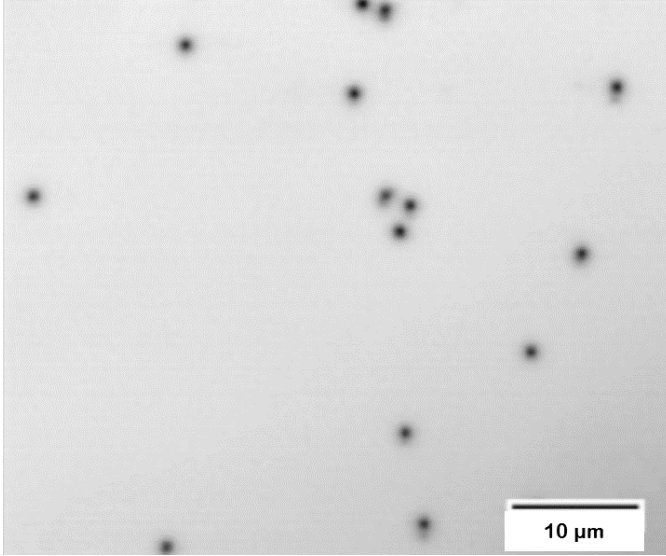


Figure 42. Confocal PL micrograph of a CdTe layer grown on (100)-oriented CdTe substrate with a dislocation density of mid- 10^5 cm^{-2} .

3.4.1.2 Growth initiation study

There are several steps involved in initiating the MBE growth of CdTe. Pre-growth annealing is one of the growth-initiation processes that is necessary for the MBE growth of II-VI compounds in order to remove oxides and carbon contaminants that might have contaminated the surface of the substrate while moving the substrate through the buffer chamber or simply as it existed after the atomic-hydrogen cleaning of the sample surface. Samples were treated with different pre-growth annealing temperatures while other growth parameters were kept unchanged. Sample z-275 was preheated to 300 °C while sample z-274 was pre-heated to 325 °C and z-276 to 400 °C. The AFM and cPL images are shown in Figures 43, 44, and 45 for a comparison of defect densities. This study suggests that a pre-heat temperature of 50 °C above the growth temperature provides reasonable lower defect density when compared to other pre-heating temperatures studied.

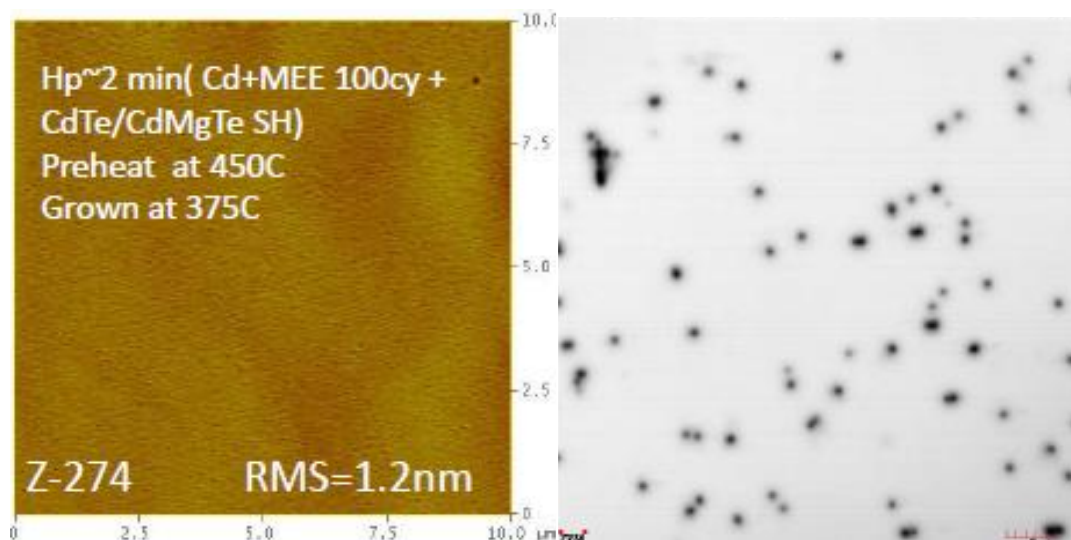


Figure 43. AFM and cPL images of sample z-274. Sample was heated at 325 °C for ten minutes prior to growth and was grown at 250 °C.

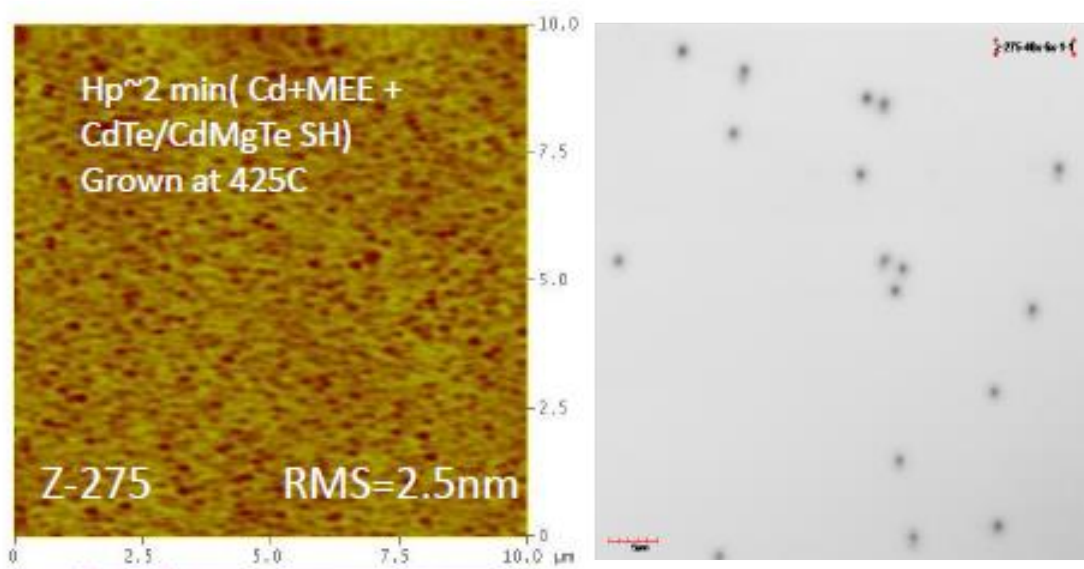


Figure 44. AFM and cPL images of sample z-275. Sample was heated at 300 °C for ten minutes prior to the growth and grown at 250 °C.

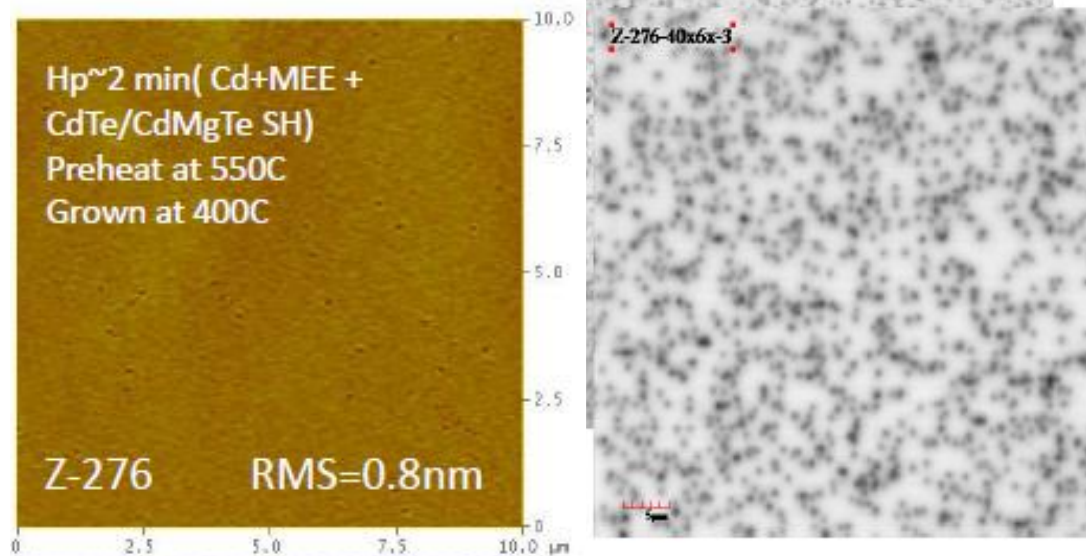


Figure 45. AFM and cPL images of sample z-276. Sample was heated at 400 °C for ten minutes prior to growth and was grown at 250 °C.

The effect of exposing the sample to Cd flux or Te flux during pre-growth annealing was studied and compared to a sample where pre-growth annealing was done without exposing either Cd or Te flux. The pre-growth annealing in all these three samples (z-243, z-246, z-247) was completed at 50 °C above growth temperature but had a different flux (Cd or Te) exposure condition during these pre-growth anneals. All other growth conditions were the same for these three samples. The AFM images and corresponding cPL images of these samples are presented in Figures 46, 47, and 48 and Table 9.

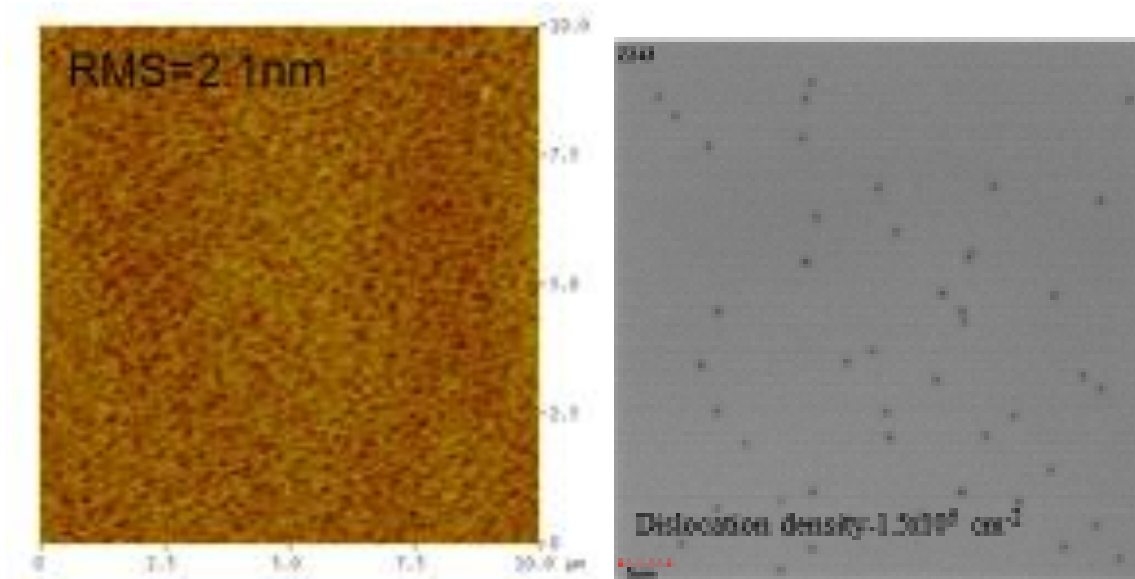


Figure 46. AFM and cPL images of sample z-243. Sample annealed with neither Cd nor Te flux exposure prior to growth.

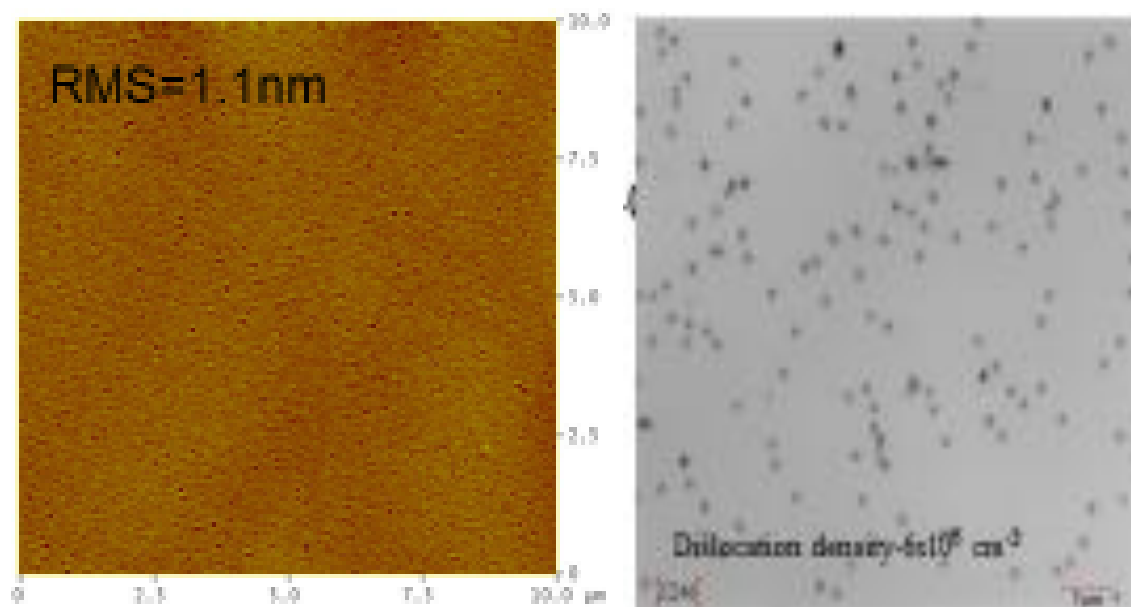


Figure 47. AFM and cPL images of sample z-246. Sample annealed with Te flux exposure prior to growth.

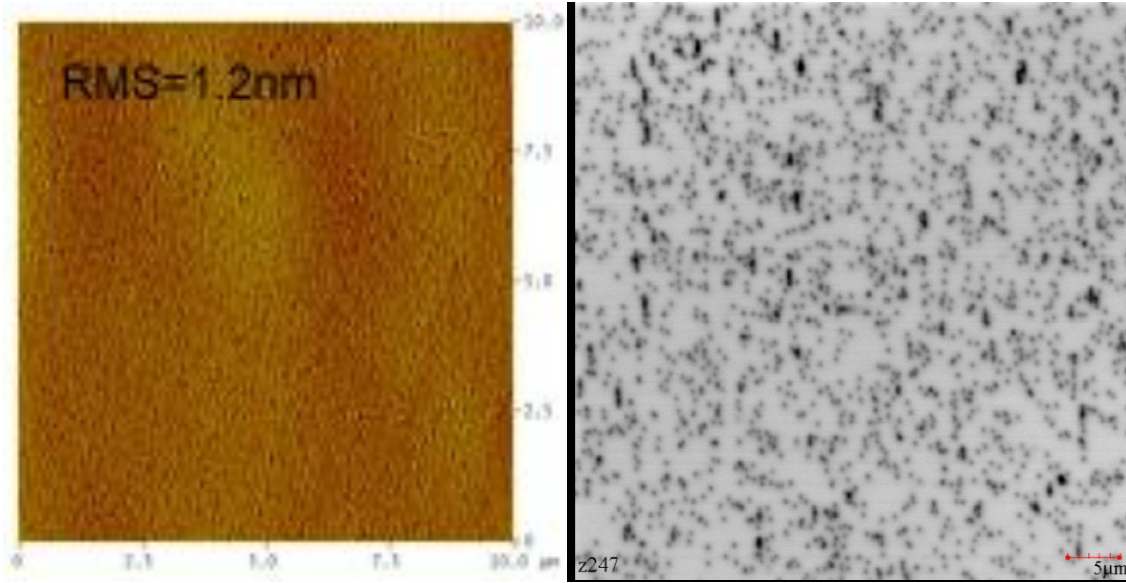


Figure 48. AFM and cPL images of sample z-247. Sample annealed with Cd flux exposure prior to growth. There is evidence of twinning defect in cPL image.

Table 9. Comparison of samples with different flux exposure conditions during pre-growth annealing.

Sample number	Flux condition during pre-growth annealing	RMS value determined by AFM (nm)	Defect density determined by cPL (/cm ²)
Z243	no flux	2.1	1.5E6
Z246	Te flux	1.1	4E6
Z247	Cd flux	1.2	4E9

Pre-growth annealing studies was extended to CdTe/CdMgTe single heterostructures (SH). Z-269 was annealed with Cd flux while z-270 was annealed without any flux. The AFM and cPL images of sample z-269 and z-270 are shown in Figures 49 and 50. The cPL image of sample z-269 shows high twin-like defect density while the cPL image of z-270 shows reasonable defect density that is comparable to samples previously annealed without any flux exposure but with less MEE cycles. Comparison of samples z-243 and z-270 suggest that fifty cycles of MEE is sufficient to meet the MEE requirement of the growth optimization procedure.

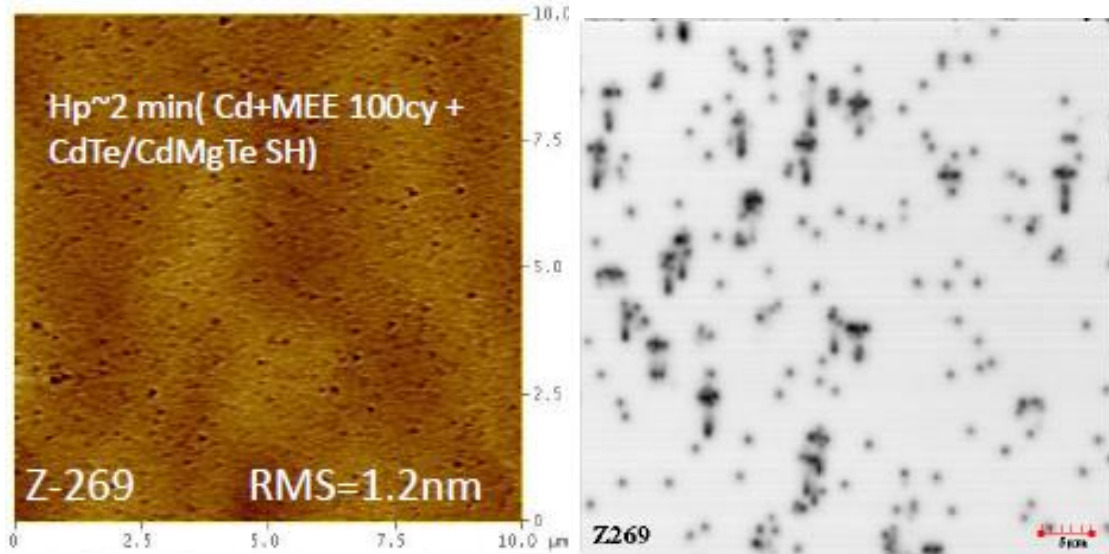


Figure 49. AFM and cPL images of sample z-269. Sample annealed with Cd flux exposure prior to growth.

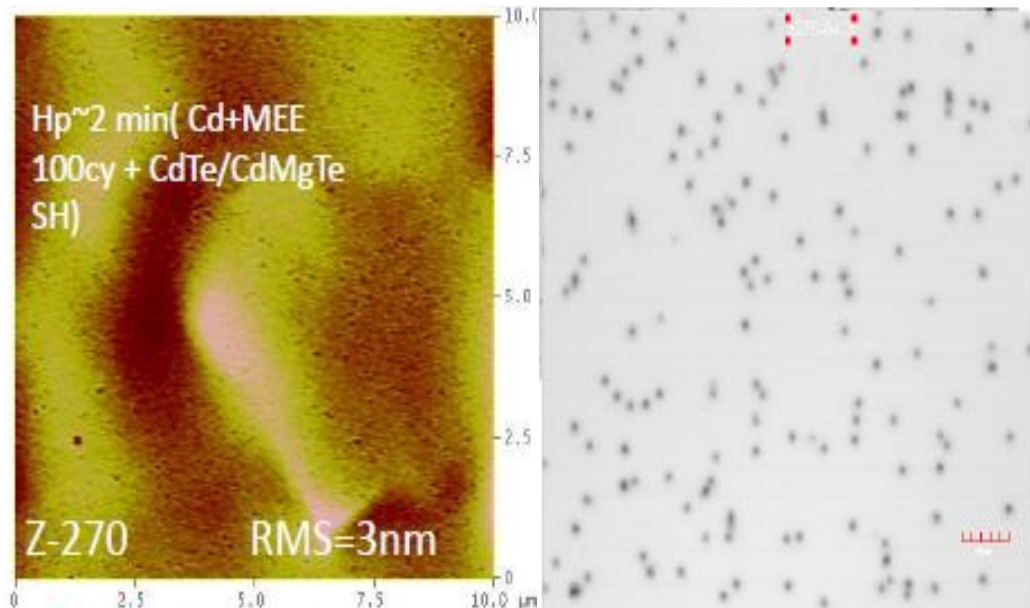


Figure 50. AFM and cPL images of sample z-270. Sample annealed with neither Cd nor Te flux exposure prior to growth.

The sample annealed without Cd or Te flux has lower defect density than the samples annealed under either Cd or Te flux during the pre-growth annealing. This study suggests that group II or VI exposure during pre-growth annealing seems to be ineffective.

3.4.1.3 Growth parameters optimization study

To corroborate the initial RHEED experiment, the study of Cd over pressure during CdTe growth in three CdTe substrates that were hand polished under the same polishing conditions suggests that 20% Cd over pressure in CdTe growth lead to a less defective structure than 10% and 40% Cd over pressures. CdTe layers were deposited on these substrates for four hours with different Cd/CdTe ratios. Figure 51 shows the AFM images for 0%, 10%, 20%, and 40% Cd/CdTe ratios. The root mean square of the surface roughness for these ratios are 3.9 nm, 3.2 nm, 0.84 nm, and 3.9 nm, respectively. Varying Cd backgrounds over pressure while growing CdTe gives smooth sample surfaces, especially with 20% Cd overpressure, which yielded the lowest surface roughness RMS and a low defect density count as reported in Table 10.

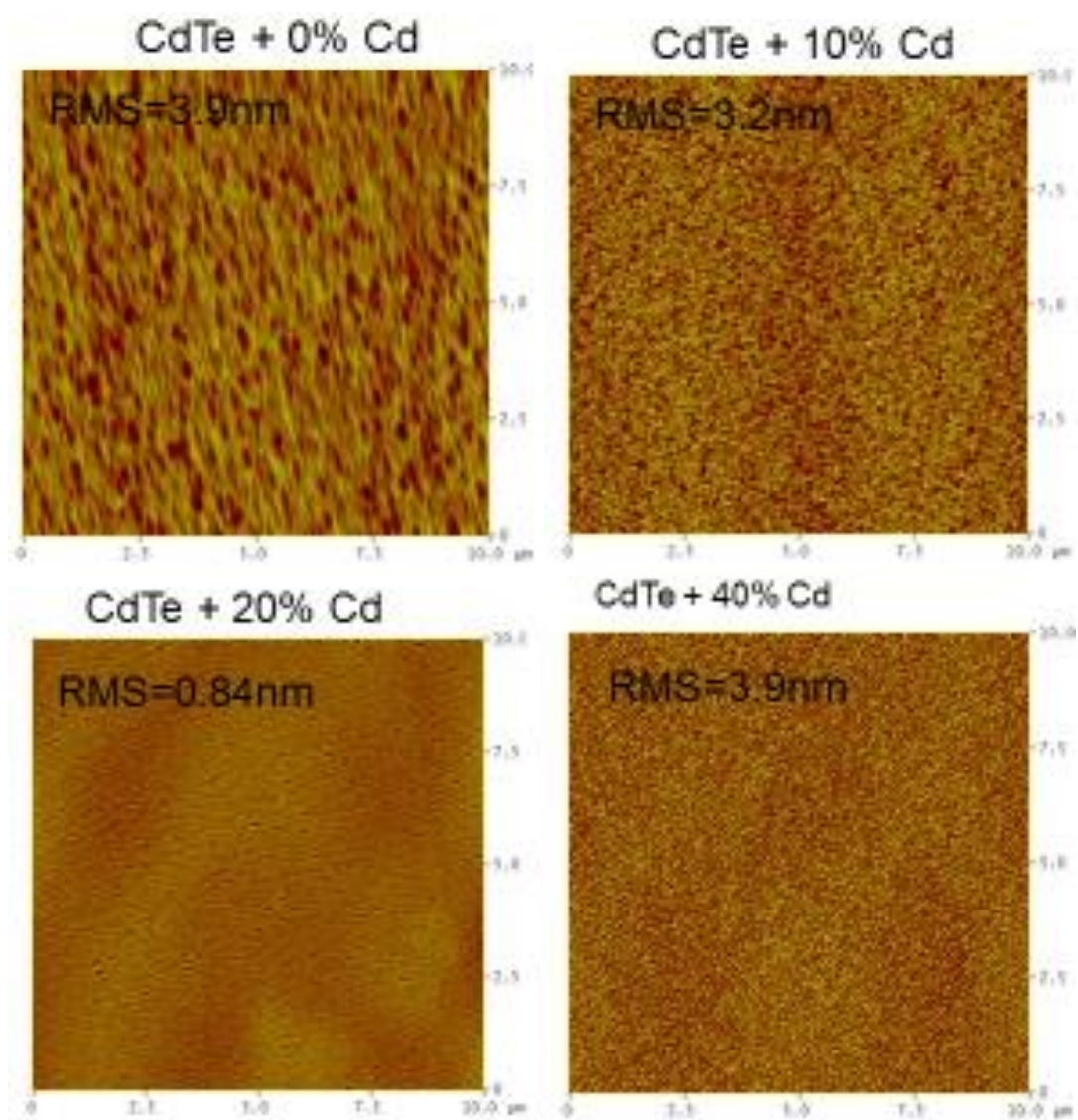


Figure 51. AFM images of CdTe samples grown at different Cd overpressure rates.

Table 10. Comparison of samples with different Cd/CdTe ratios.

Sample number	Cd/CdTe ratio (%)	RMS value determined by AFM (nm)	Defect density determined by cPL (/cm ²)
Z238	0	3.9	6E6
Z239	10	3.2	-
Z240	20	0.84	3E6
Z249	40	3.9	

3.4.2 Optical characterization – photoluminescence and TRPL

For optical studies, double heterostructures of CdMgTe/CdTe, where CdTe is placed between two CdMgTe barrier layers to passivate the CdTe surface on both sides, and single heterostructures of CdZnTe, CdZnSe and CdMgTe were analyzed. The normalized PL efficiency of undoped CdTe/CdMgTe double heterostructure (DH) is compared to that of single heterostructures (SH) as shown in Figure 52. Normalized PL efficiency was achieved by dividing the PL signal by the excitation intensity. CdMgTe barriers have an order of magnitude higher PL efficiency than CdZnTe and CdSeTe barriers, which is similar to the report of Seyedmohammadi et al.⁸² where CdTe/CdMgTe double heterostructures are shown to have a higher PL intensity than CdTe/CdZnTe double heterostructures. Also, DHs have at least two orders of magnitude higher PL efficiency than the SHs.

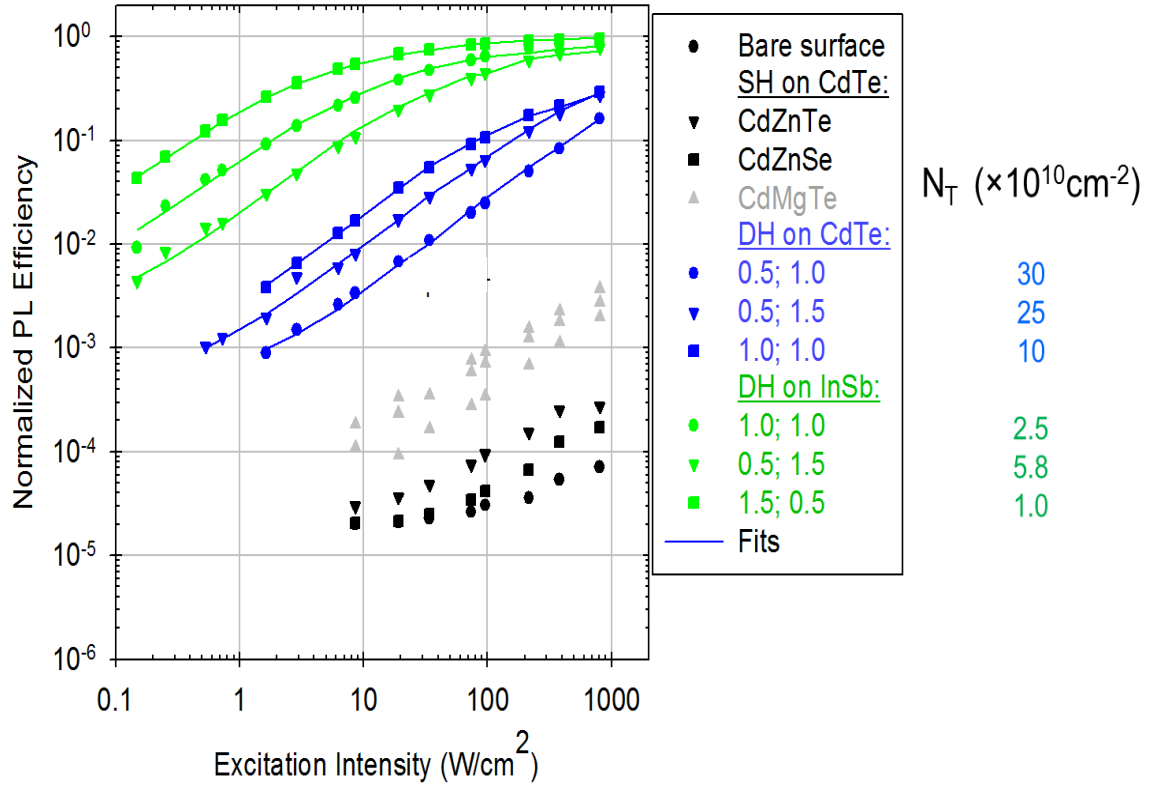


Figure 52. The normalized PL efficiency of single-sided barriers (SH), two-sided CdMgTe barriers (DH) on CdTe substrates, and DH growth on InSb substrates. The buffer layer thickness (μm), the absorber layer thickness (μm), and the resulting trap density (10^{10}cm^{-2}) are indicated for each DH.¹⁰²

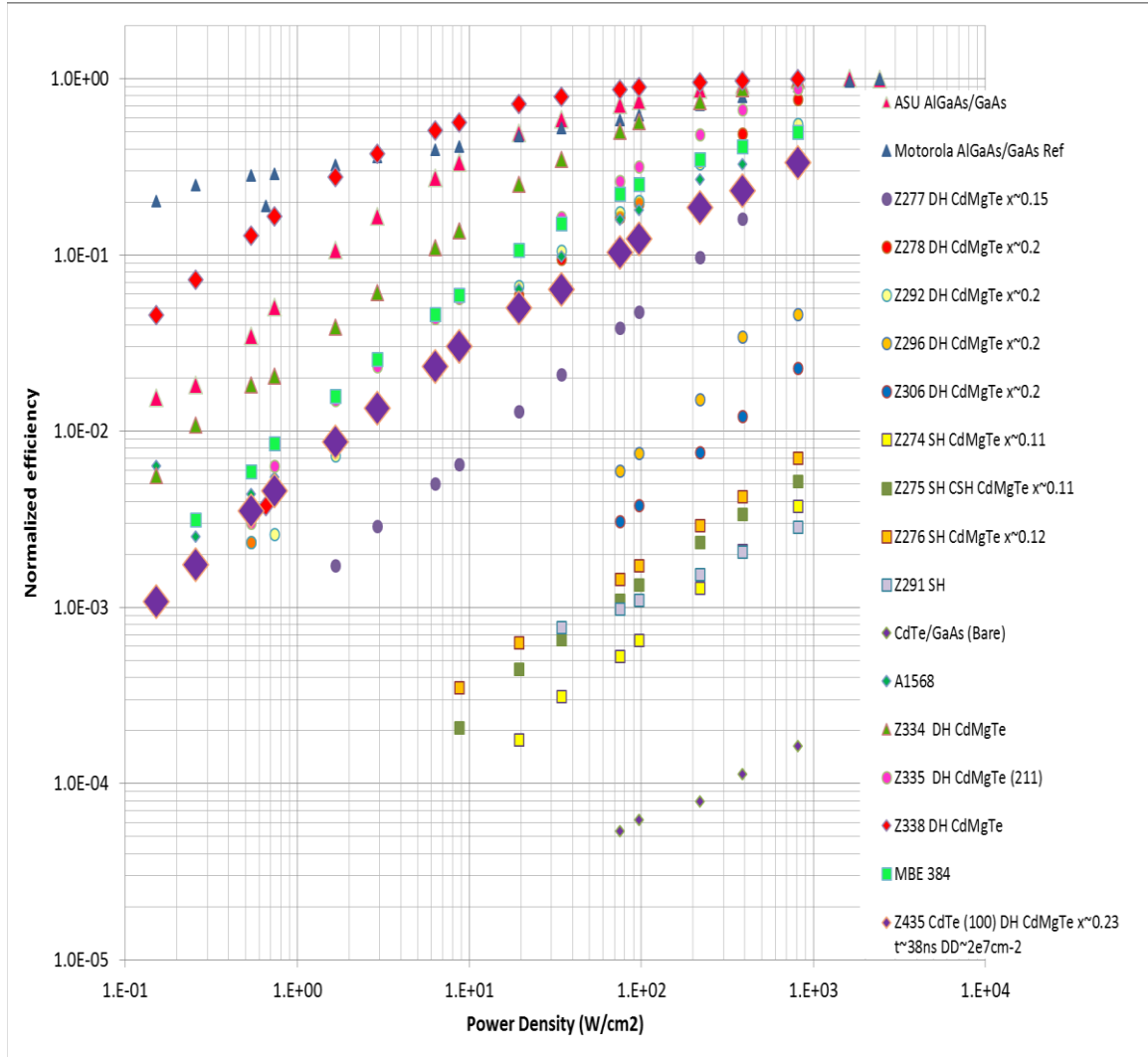


Figure 53. PLI for CdTe/CdMgTe DHs and SHs grown on InSb and CdTe substrates with various Mg concentration. ASU AlGaAs/GaAs and Motorola AlGaAs/GaAs are reference samples. Sample z435 is a DH grown on (100)-oriented CdTe substrate while samples z277, z278, z292, z296, and z306 are DHs grown on (211)-oriented CdTe substrate. Samples z274, z275, z276, and z291 are SHs grown on (211)-oriented CdTe substrate. Samples z334, z338, and MBE 384 (grown at First Solar Inc.) are DHs grown on (100)-oriented InSb substrate while sample z335 is a DH grown on (211)-oriented InSb substrate.

For this project, PLI of SH and DH structures were compared for different substrates (CdTe and InSb) and different orientations (100 and 211) as shown in Figure 53. The PLI of DHs grown on a (100)-oriented CdTe substrate seems to be at least $\sim 2\times$ higher in PLI than layers grown on (211)-oriented CdTe substrates while DHs grown on

(100)-oriented InSb substrates produced $\sim 1.1\times$ higher PLI than layers grown on (211)-oriented InSb substrates. In general, CdTe/CdMgTe DHs grown on InSb substrates have $\sim 3\times$ higher PLI than DHs of a similar structure grown on CdTe substrates due to the decreased number of dislocation defects in structures grown on InSb as quantified by cPL. Also, PLI of structures with thicker buffer layers show slightly higher PL intensity than samples with a similar structure but with thinner buffer layers because thicker buffer layers are inclined to reduce interfacial trap density.

To examine the influence of Mg content on PLI, Mg content in CdTe/Cd_{1-x}Mg_xTe DHs grown on (100)-oriented InSb substrates varied from 0.23 x value to 0.46 x value, and samples with approximately 0.35 x value yielded the highest PL intensity as shown in Figure 54. It is noted that the PL intensity for $x\sim 0.28$ to $x\sim 0.35$ is comparable. The critical layer thickness of Cd_{0.65}Mg_{0.35}Te was estimated based on the Matthews and Blakeslee model to be around 37 nm.¹⁰⁰ Subsequently, CdMgTe/CdTe double heterostructures were designed with bottom and top barrier thicknesses of 30 nm. Growth temperature and growth initiation parameters at this Mg composition were further determined to gain higher PL intensity and less dislocation density in CdTe/CdMgTe structures.

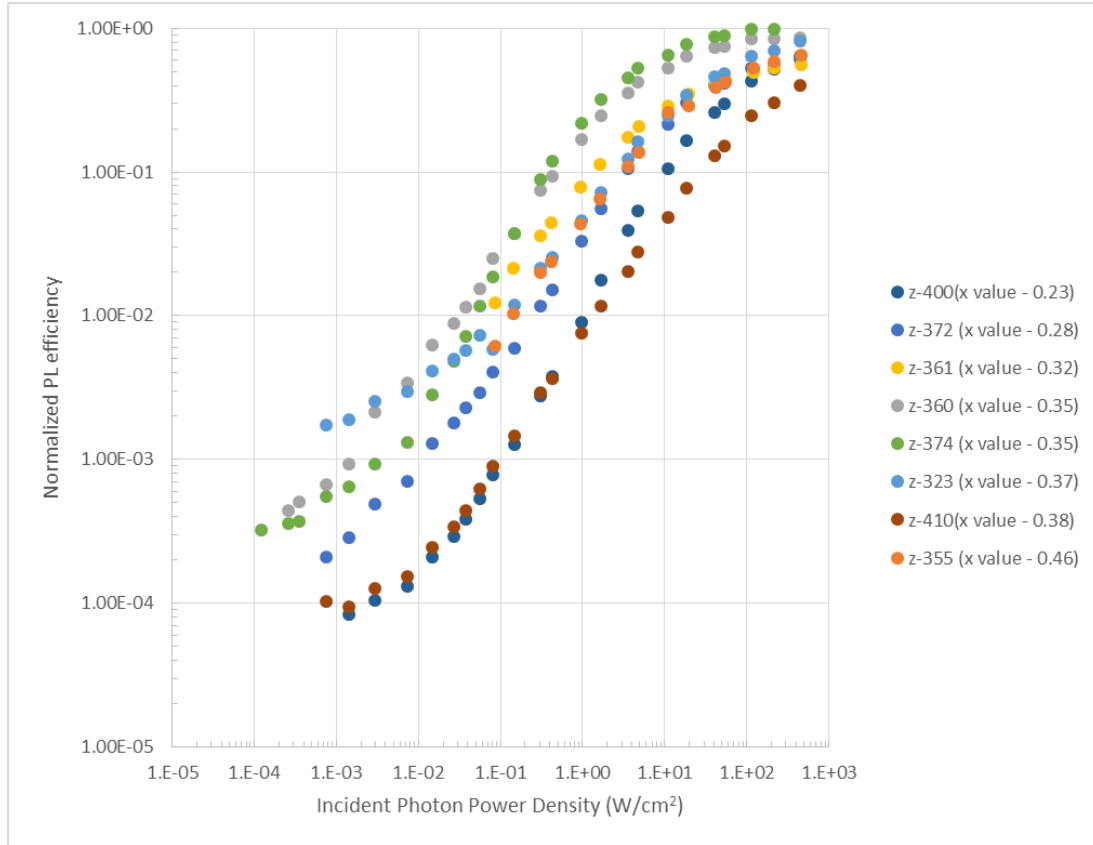


Figure 54. PLI for CdTe/CdMgTe DH grown on (100)-oriented InSb substrates with various Mg concentration.

PLI and TRPL lifetime depend on surface (or bulk) recombination. As shown in Figure 55, lifetime increases with CdMgTe passivation as seen in the case of single heterostructures and double heterostructures. Also, carrier lifetime increases with improving surface interface quality, which tends to affect overall defect density as was the case for double heterostructures grown on InSb substrates as they have higher surface quality than CdTe substrates.

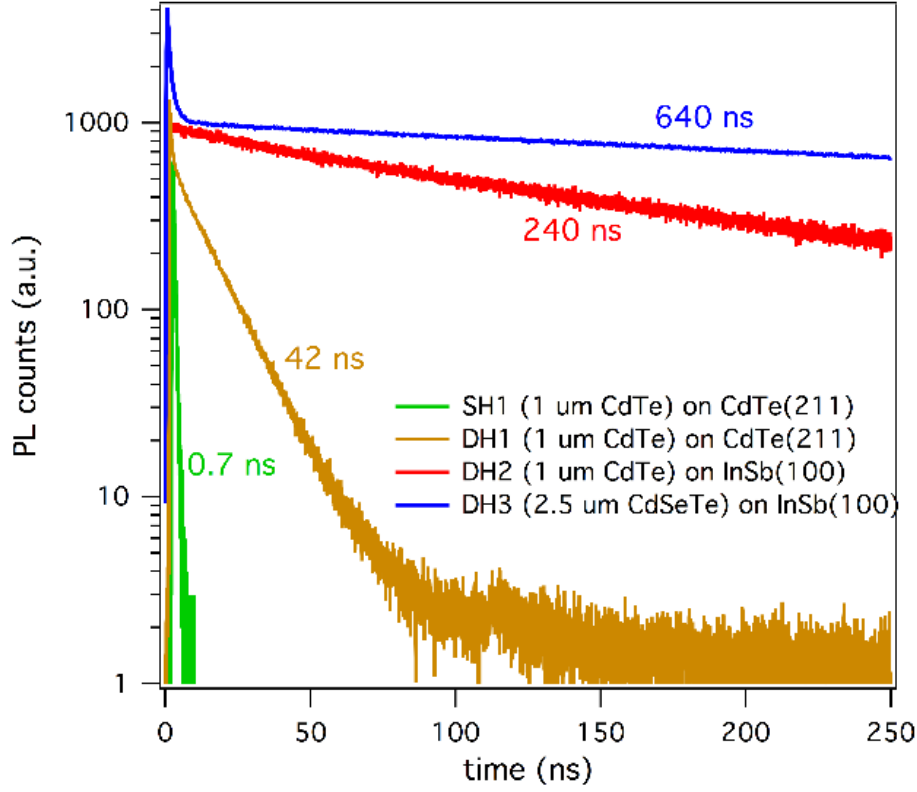


Figure 55. TRPL data representation showing lifetimes increasing with CdMgTe passivation and improving substrate interface quality.

The TRPL measurements were done in the low injection regime to mitigate the complexity of dealing with multiple exponential decay, so reliable lifetime numbers were obtained and used to estimate surface recombination velocity (SRV). In undoped CdTe/CdMgTe D.H, assuming the effect of radiative recombination is negligible, then effective lifetimes is given as

$$\frac{1}{\tau_{eff}} \approx \frac{1}{\tau_{SRH}} + \frac{2S}{d} \quad (3.8)$$

The equation above can be used to calculate the SRV and SRH lifetime from a given TRPL data if the absorber thicknesses are known.

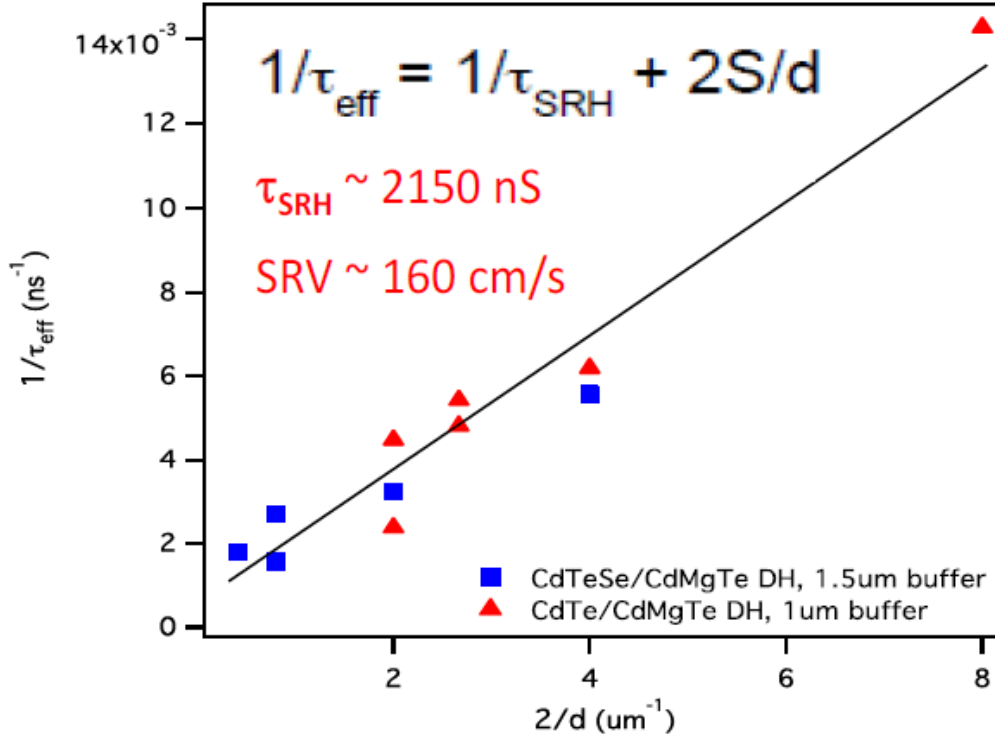


Figure 56. TRPL of undoped CdTe/CdMgTe and CdSeTe/CdMgTe DHs.

Lifetime measurements were taken in DH samples with varying absorber thicknesses but with similar CdMgTe barriers in order to determine SRH lifetime and SRV. The graph shown in Figure 56 is showing the plot of the reciprocal of TRPL lifetime versus the reciprocal of the absorber thickness. The intercept of the straight line fit at high thickness is used to estimate the bulk lifetime to be ~2150 ns while the recombination velocity, which is estimated from the slope of the graph, is ~160 cm²/s for these undoped DHs.

3.5 Summary

CdTe and CdTe alloys were studied for optimal growth conditions. Growth rate was determined at various substrate temperatures using InSb and CdTe substrates in order to derive the temperature window for the CdTe growth processes. The effect of

temperature on the growth rate of CdTe was studied over a temperature range of 210 °C to 400 °C while growth rate and RHEED reconstruction were used to determine the stoichiometric point. It was observed that 20% Cd overpressure is sufficient to achieve stoichiometric conditions.

Based on the results of the studies aimed at optimizing the growth process, the best practices for optimal growth conditions for CdTe and its alloys are summarized in the following steps.

1. Polish the surface of CdTe and CdZnTe substrates; surface polishing with Br-methanol etching and DI water rinsing is exceedingly important to remove polishing damage from the surface of as-received samples.
2. Perform hydrogen cleaning on polished CdTe and CdZnTe substrates. Hydrogen cleaning is needed for the removal of surface contaminants.^{91, 92, 103}
3. Anneal hydrogen-cleaned substrates. Pre-growth annealing (50 °C above growth temperature) for ten minutes is helpful in removing oxides from the surface of the sample that might have occurred while transferring samples from the hydrogen chamber to growth chamber. Studies reveal that a Cd or Te treat during this pre-growth annealing is not helpful.
4. Expose the surface of the annealed substrates to Cd flux for one minute before MEE.
5. Perform MEE for twenty to fifty cycles.
6. Grow CdTe-related structures on the substrates with 20% Cd over pressure.

Growth rate is 0.4 MLs⁻¹.

These optimized growth conditions were used for the MBE growth of most of the undoped and doped samples. Samples grown on InSb substrates were used to determine properties that can be achieved with MBE-grown CdTe. Semi-automatic polishing is effective in removing mechanical polishing damage in as-received CdTe and CdZnTe substrates. C-PL was used to quantify dislocation content and dislocation and twin-related defects were observed for the different orientations. Twin-related defects were suppressed in (211)B-orientated substrates. Defect densities varying from 10^4 to 10^7 cm⁻² were observed in structures grown on InSb substrates while defect densities varying from 10^5 to 10^7 cm⁻² were observed in structures grown on CdTe substrates. The removal of polishing damage in CdTe and CdZnTe substrates reduced defect density by almost two orders of magnitude. Generally, very low dislocation density and twin content can be achieved for epitaxial CdTe. Using PLI to evaluate the surface and interface quality of the grown CdTe structures, it was observed that the reduction of dislocation density from 10^7 cm⁻² in CdTe layers without a CdMgTe barrier layer to block surface recombination yielded only slight improvement in PL intensity.

Double heterostructures were used to study surface and interfacial recombination, which could have negative impact on open-circuit voltage, a key parameter for CdTe solar cells⁷⁹. In this study, PL intensity variation was recorded as the laser intensity was varied with a series of calibrated neutral-density filters. The PLI efficiency was normalized by dividing the PL intensity by the excitation intensity in order to obtain a dependence of PL on excitation as a horizontal line. Interfacial trap density was extracted by modeling the experimental PLI data and the assumption of $B_{rad} = 10^{10}$ cm³/s worked well in fitting the data.

CPL and PLI results suggest that unpassivated CdTe films with dislocation densities varying from 10^4 to 10^7 cm^{-2} will likely have nearly identical PLI results, consequently indicating that the unpassivated surface of CdTe could be a significant recombination factor. The use of $\text{Mg}_{1-x}\text{Cd}_x\text{Te}$ barriers with composition $x \sim 0.35$ in CdMgTe/CdTe double heterostructures resulted in high PL efficiency for CdTe, comparable to the efficiency observed for AlGaAs/GaAs DH, indicating that they are exceptionally effective at reducing recombination at the surfaces and interfaces of CdTe. DHs with varying thicknesses were used to assess the contribution of the interface to recombination. Observation of select DHs revealed that increase in the absorber-layer thickness resulted in improved PLI, but the extracted interfacial trap density for the studied DHs was similar. Buffer layer thickness was also varied to further study the impact of interface on recombination in CdTe, improved PLI results, and reduction of interfacial trap density with increase in buffer thickness, indicating that buffer thickness has more impact on interfacial recombination than absorber thickness. When the buffer layer's thickness was increased from $0.5 \text{ }\mu\text{m}$ to $1.0 \text{ }\mu\text{m}$ on CdTe substrates and the absorber thickness remain unchanged, the PLI efficiency for the $1.0 \text{ }\mu\text{m}$ -thick absorber improved by a factor of two, and the interfacial trap density decreased by a factor of three. Also, a buffer layer thickness increase on InSb substrates resulted in a PLI increase at excitation intensity $\leq 100 \text{ W/cm}^2$ and an interfacial trap density decrease, suggesting an interaction with the substrate/epilayer interface. A $1.5 \text{ }\mu\text{m}$ -thick buffer with a $0.5 \text{ }\mu\text{m}$ absorber layer on an InSb substrate yielded the highest PLI observed so far in any CdTe-based structure with interfacial trap density of $1 \times 10^{10} \text{ cm}^{-2}$, which is comparable to the highest quality AlGaAs-GaAs DHs. InSb substrates used as alternatives to possible

surface preparation issues with bulk CdTe to grown CdTe structures show a higher PLI by a factor of five than the PLI of a similar structure grown on CdTe. Increase in TRPL lifetime tends to track increase in PLI of CdTe films, as would be predictable from a decrease in non-radiative recombination. Bulk carrier lifetimes up to 2150 ns and a surface recombination velocity less than $200 \text{ cm}^2/\text{s}$ in these MBE-grown double heterostructures was achieved.

4. DOPING OF CdTe

4.1 Introduction

Intentional impurities, also known as dopants, can be incorporated into a semiconductor system in order to control conductivity. The desired location of an impurity atom in the crystal lattice of a compound semiconductor is in the substitutional lattice sites, which can either be a cation or anion site. Factors that determine which site the impurity atom resides in are valence electron correlation, size of impurity, and bond strength.

In many semiconductor devices, having good conductivity is highly desirable, which usually calls for incorporating a high concentration of dopants. It is important to note that some characteristics, such as ionization energy, fundamental absorption edge, density of state in the vicinity of band edges, and energy of the fundamental gap of the semiconductor device, can change as a result of the effects high doping concentration generate.⁶⁷

There are several ways of incorporating dopant atoms onto host semiconductors—CdTe and CdMgTe—meaning that there are several ways of inserting dopant atoms into the desirable substitutional site. The most commonly used techniques of doping semiconductors are epitaxial crystal growth, ion implantation, and diffusion.

Some of the commonly used epitaxial growth techniques for incorporating dopants are molecular beam epitaxy, organometallic vapor phase epitaxy, and liquid phase epitaxy. Although the principles governing the growth process might be different, the law of mass action can be applied to analyze the characteristics of the dopant incorporation process, such as temperature and flux ratio.

Another technique for incorporating impurity is by ion implantation. This technique incorporates dopants by accelerating charged dopants in an electric field toward a semiconductor target. Doping can be controlled with lateral selectivity in using this technique.

The process of accelerating dopant atoms can cause structural damage to the semiconductor target, but the effect can be reduced by high temperature annealing to ensure decent electrical properties. The major drawback of this technique is the characteristic width of the doping distribution. The doping concentration is given as

$$N(z) = \frac{N^{2D}}{\sqrt{2\pi}\Delta R_P} \exp \left[- \left(\frac{z-R_P}{\sqrt{2}\Delta R_P} \right)^2 \right] \quad (4.1)$$

where N^{2D} is the density of implanted ions per cm^2 .⁶⁷

Dopants can also be incorporated using a diffusion technique. This is done by using a surface reservoir to diffuse dopants into the bulk of the host material. It is difficult to determine the shape of the doping profile, making doping incorporation by ion implantation and epitaxial growth more beneficial.⁶⁷ The potential structural damage from ion implantation during incorporation has made epitaxial growth more applicable in this process.

Maximum doping concentration is an important characteristic of dopants, and it is of interest because it can help in determining doping efficiency. The ratio of carrier concentration to dopant concentration is referred to as doping efficiency, which is desired to be close to uniform. Often times, high doping efficiency is hard to achieve due to some limiting factors. The fundamental limits of maximum attainable doping concentration depend on the dopant element, the host semiconductor, and the doping technique. Some

of the mechanisms responsible for doping efficiency limits are compensation, solubility limit, elastic strain, and diffusion.⁶⁷

Compensation is the phenomenon where doping gives rise to a generation of opposite carriers, thereby reducing the net-free carriers. This limits the doping efficiency and is undesirable in most cases. The maximum concentration of dopant atoms that can be incorporated into a host semiconductor so that they are distributed homogeneously without clustering is referred to as solubility limit. Beyond this limit, not all dopants will be electrically active. Techniques like TEM and APT can be used to determine the presence of precipitates in a doped semiconductor. It has been suggested that the solubility limit depends on growth conditions, thereby making it difficult to establish a certain limit for a dopant element in a host semiconductor without considering the specific growth conditions. Elastic strain can be a limiting mechanism for dopant concentration if strain increases as doping concentration increases. Compressive or tensile strain can occur when the atomic size of the dopant element is different from the atomic size of the host atom.⁶⁷

In this project, MBE was used to incorporate dopant atoms into CdTe. MBE growths of doped CdTe samples were performed by varying the growth conditions, such as pre-growth annealing, migration enhanced epitaxy (MEE), growth temperature, flux ratios, and growth rate, to determine optimal growth conditions and to understand how these conditions affect dopant incorporation. The main objective here is to optimize dopant incorporation in order to achieve dopant concentration needed to fabricate efficient solar cells. For efficient solar cells, the p-type absorber layer is expected to have a doping concentration $\geq 10^{16} \text{ cm}^{-3}$ while an n-type layer is expected to have a doping

concentration that is at least an order of magnitude higher than the doping concentration of the p-type absorber layer.¹⁰⁴

4.2 CdTe:I and CdMgTe:I

Iodine doping was done with the use of ZnI₂ as the solid source since elemental halogens are not compatible with the molecular beam epitaxy (MBE) process due to their high vapor pressures. A dual-zone low-temperature effusion cell was used for this ZnI₂ source, which was constantly kept under the flow of chilled water to keep the temperature of the ZnI₂ below 10 °C when not in use to limit sublimation and background I.

4.2.1 Experimental details

The ZnI₂ oven temperature was calibrated for iodine concentration in order to have better control over the number of atoms incorporated during the doping process. Figure 57 shows a calibration sample (z-396), which was grown with different ZnI₂ oven temperatures for different doped layers that have undoped spacers in between them. Brun-Le-Cunff et al.²⁸ achieved maximum doping of $6.2 \times 10^{18} \text{ cm}^{-3}$ on I-doped CdTe grown on (100) Cd_{0.96}Zn_{0.04}Te with the ZnI₂ cell temperature set at 120 °C, but they did not examine Iodine incorporation at higher temperature values. This study examined dopant incorporation in I-step-doped CdTe on (100) InSb by varying ZnI₂ cell temperature at 80 °C, 120 °C, 140 °C, and 160 °C as shown in Figure 57. Each step-doped layer is 200 nm thick while each spacer between the step-doped layers is also 200 nm thick. Maximum doping of $2 \times 10^{19} \text{ cm}^{-3}$ was achieved at ZnI₂ cell temperature of 160 °C.

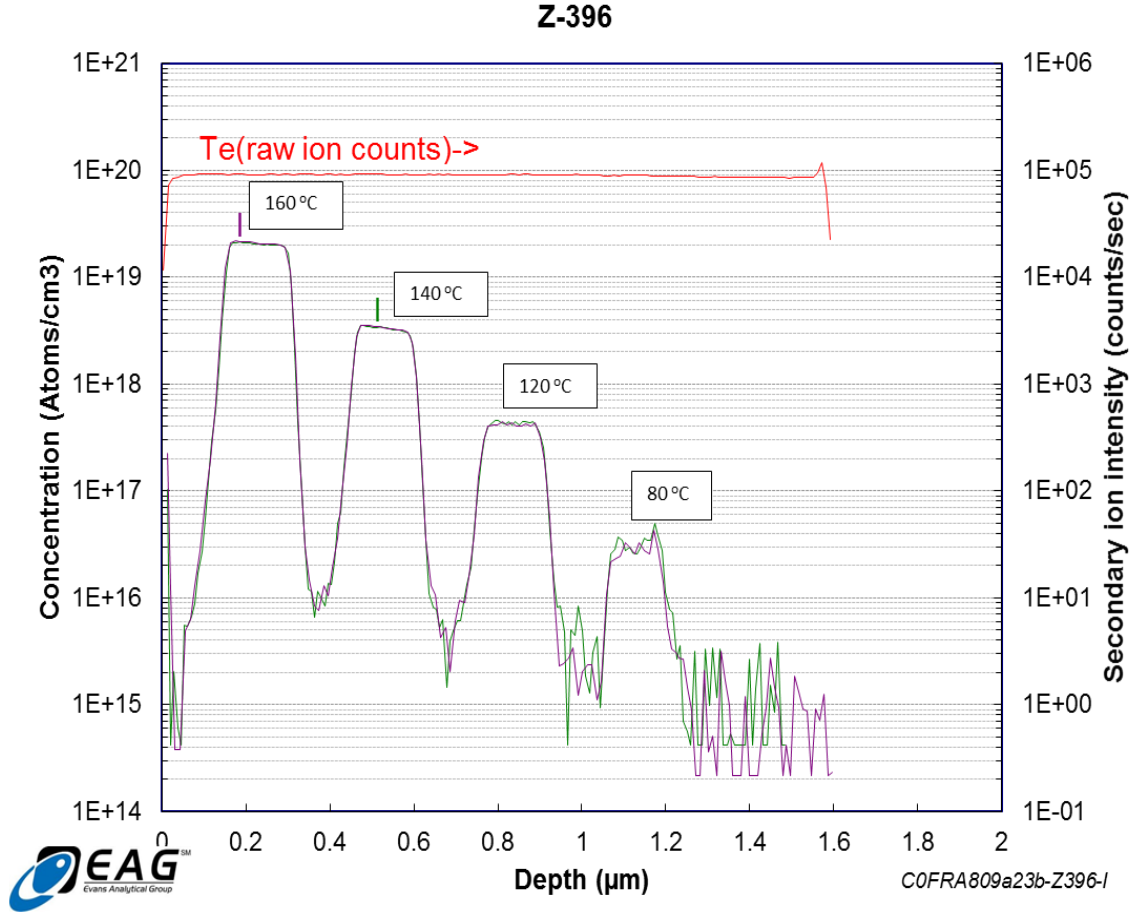


Figure 57. SIMS profile of z396 showing different cell temperature growth for doping concentration calibration.

One relationship between the effusion cell temperature of ZnI_2 and its vapour pressure is given as ¹⁰⁵

$$P = 10^{\left[18.397 - \frac{7578}{T} - 2.21(\log T)\right]} \quad (4.2)$$

Vapour pressures of different temperatures were calculated using equation 4.5, and the result was used to extrapolate concentration of the dopant. The temperature variation SIMS measured concentration coincides well with the values estimated from the calculated vapor pressures at higher temperatures as shown in Figure 58, but it varies at

lower temperatures. The SIMS calibration serves as the basis for I doping calibration in the subsequent doping experiment.

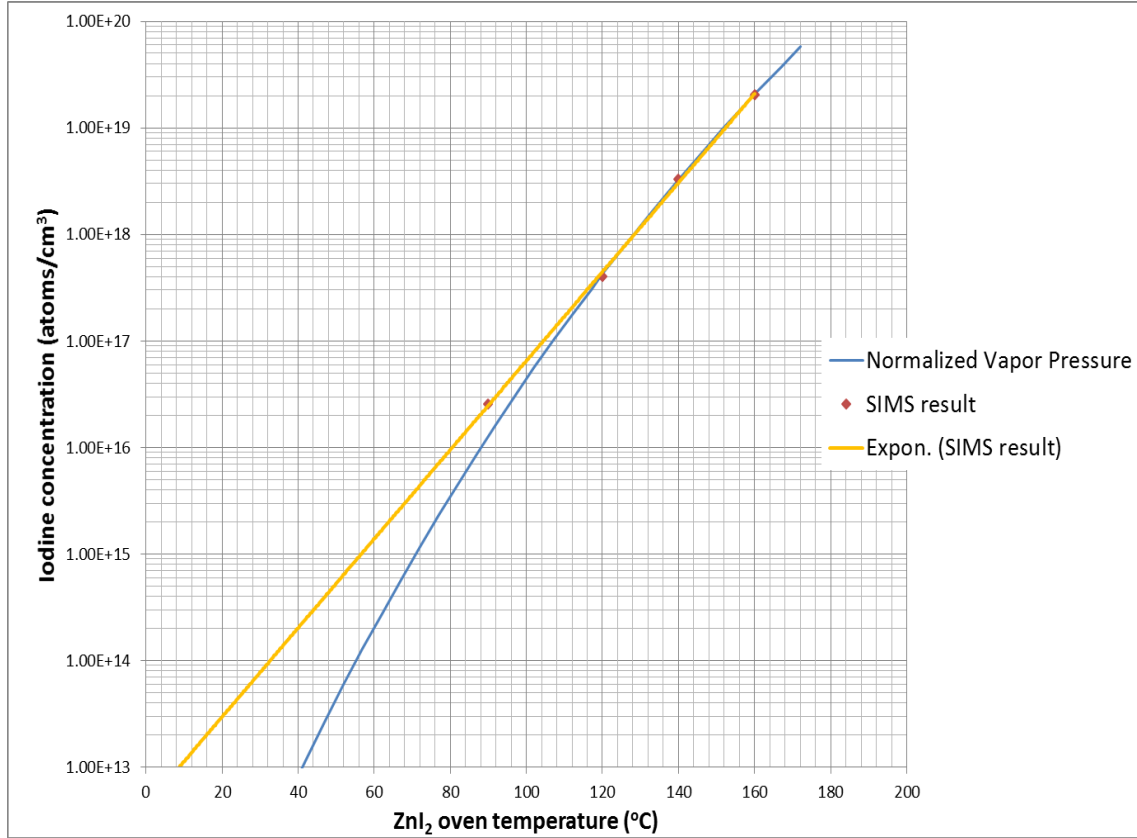


Figure 58. Temperature-dependent Iodine concentration for Iodine doping calibration.

I-doped CdTe single and double heterostructure samples were grown on CdTe and InSb substrates at different doping concentrations based on this calibration, and the results were studied. Iodine incorporation was measured at EAG Laboratories with secondary ion mass spectrometry (SIMS). Ion implant standards were fabricated to allow accurate quantification of I in CdTe. SIMS measurement of I-doped layers was consistent with the estimation of the doping concentration calibration that was initially done. Carrier concentration of some of the grown iodine-doped samples were measured with the Hall

measurement technique at room temperature and compared to their corresponding I concentration as measured by SIMS in order to measure the doping efficiency.

I-doped CdMgTe films were also grown in order to study iodine doping in CdMgTe layers, which are intended to be used as barrier layers in CdTe/CdMgTe double heterostructures. The wide band gap $\text{Cd}_{1-x}\text{Mg}_x\text{Te}$ barriers, which are made to confine photocarriers and prevent parasitic rapid recombination at the CdTe surface, have a thickness of 30 nm and a composition of $x \sim 0.35$, as measured by spectroscopic ellipsometry.¹⁰⁶ These CdTe/CdMgTe double heterostructures were used for PL studies while CdTe/CdMgTe single heterostructures were grown for Hall measurement studies. For these CdTe/CdMgTe single heterostructures, semi-insulating $\text{Cd}_{0.96}\text{Zn}_{0.04}\text{Te}$ (100) substrates were used and 100-nm CdTe buffers were grown before depositing 1- μm $\text{Cd}_{1-x}\text{Mg}_x\text{Te}$ films by MBE. Mg composition was varied from $x \sim 0$ to $x \sim 0.35$. At an Mg composition of x up to ~ 0.35 , the lattice mismatch between $\text{Cd}_{1-x}\text{Mg}_x\text{Te}$ films and $\text{Cd}_{0.96}\text{Zn}_{0.04}\text{Te}$ (100) substrates is much lower than the lattice mismatch between $\text{Cd}_{1-x}\text{Mg}_x\text{Te}$ films and CdTe (100) substrates. For an Mg composition of $x \sim 0.35$, the lattice mismatch of CdTe/ $\text{Cd}_{0.65}\text{Mg}_{0.35}\text{Te}$, which is $\sim 0.34\%$, is three times larger than the lattice mismatch of $\text{Cd}_{0.96}\text{Zn}_{0.04}\text{Te}/\text{Cd}_{0.65}\text{Mg}_{0.35}\text{Te}$, which is $\sim 0.11\%$. Generally, in all these CdMgTe-related structures, the CdMgTe film was shielded against oxidation by growing a 10-nm cap layer of CdTe on the CdMgTe layer. The substrate temperature was maintained at 240 °C.

After growth, iodine-doped films of CdTe and CdMgTe were electrically characterized by the van der Pauw Hall effect technique using soldered indium as contacts. A few samples were measured as a function of temperature, which could vary as

much as 20 to 400 K. Dopant incorporation was compared to carrier concentration in some of the grown samples to determine the doping efficiencies of iodine in CdTe and CdMgTe. Using the data from some of the samples with temperature-dependent carrier concentration measurements and assuming that there was no compensation, activation energy analysis was carried out by fitting the data to the charge balance equation.¹⁰⁷

4.2.2 Results

In this study, heavy doping in CdTe at levels up to $7.4 \times 10^{18} \text{ cm}^{-3}$ with iodine was easily and reliably achieved as shown in Figure 59. Also shown in this figure is iodine doping of $\text{Cd}_{1-x}\text{Mg}_x\text{Te}$ with $x \sim 0.3-0.35$. It appears to be a good dopant in $\text{Cd}_{1-x}\text{Mg}_x\text{Te}$ with reasonable activation for n up to about $2 \times 10^{17} \text{ cm}^{-3}$ at an I concentration of about $\sim 5 \times 10^{17} \text{ cm}^{-3}$. This result suggests that compensation may be occurring at an iodine-dopant concentration above $\sim 7 \times 10^{18} \text{ cm}^{-3}$ in CdTe and $\sim 1 \times 10^{18} \text{ cm}^{-3}$ in $\text{Cd}_{0.65}\text{Mg}_{0.35}\text{Te}$.

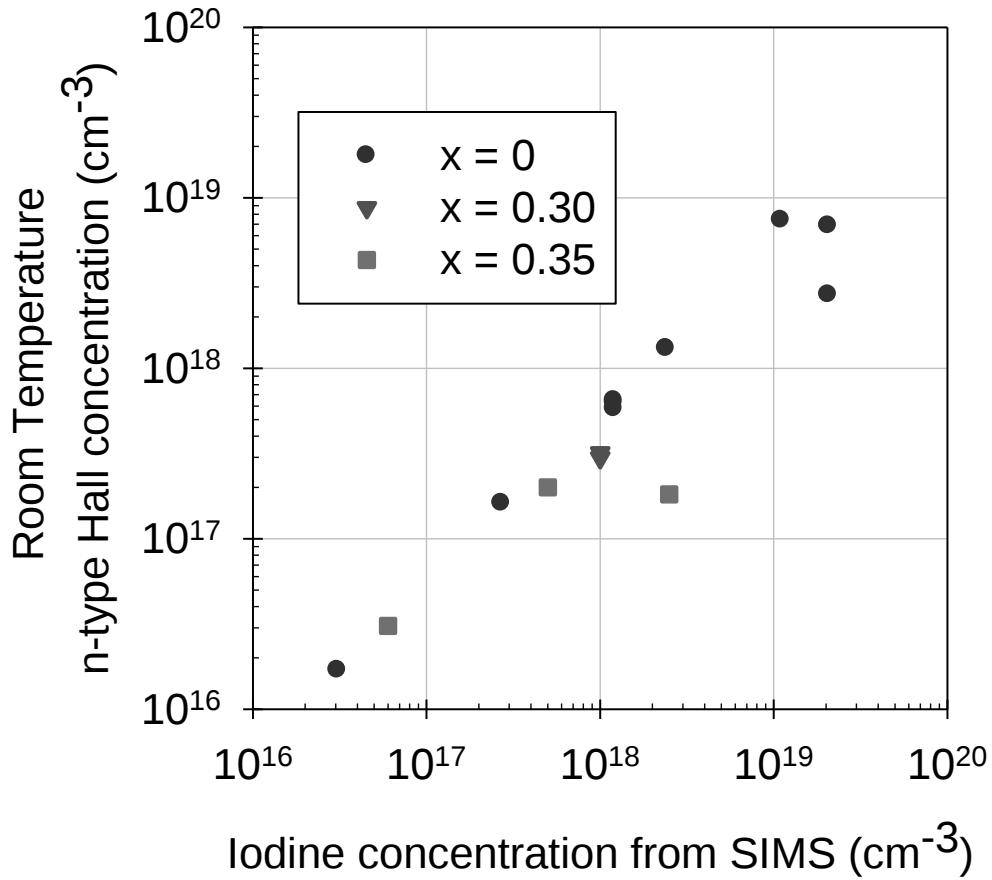


Figure 59. Electron carrier concentration at 300K vs. calibrated SIMS iodine concentration for iodine-doped CdTe and Cd_{1-x}Mg_xTe, illustrating the high level of activation and wide range of electron concentration.

Room temperature Hall measurements show that I-doped CdTe has up to 80% of its carriers active. Consistent with this, temperature-dependent Hall measurements indicated a low activation energy: ~6 meV for heavily doped samples as indicated in Figure 60. The room temperature mobility was 800 cm²V⁻¹s⁻¹, which is consistent with the highest values reported elsewhere for *n*-CdTe.¹⁰⁸ Carrier mobility increased with decreasing temperatures as shown in Figure 61. Also shown in this figure is the mobility for Cd_{1-x}Mg_xTe, which was observed to decrease with an increasing *x* value decreasing by a factor of 2 for *x*~0.3 and then falling precipitously to a room-temperature value of 38 cm²V⁻¹s⁻¹ at *x*~0.35.

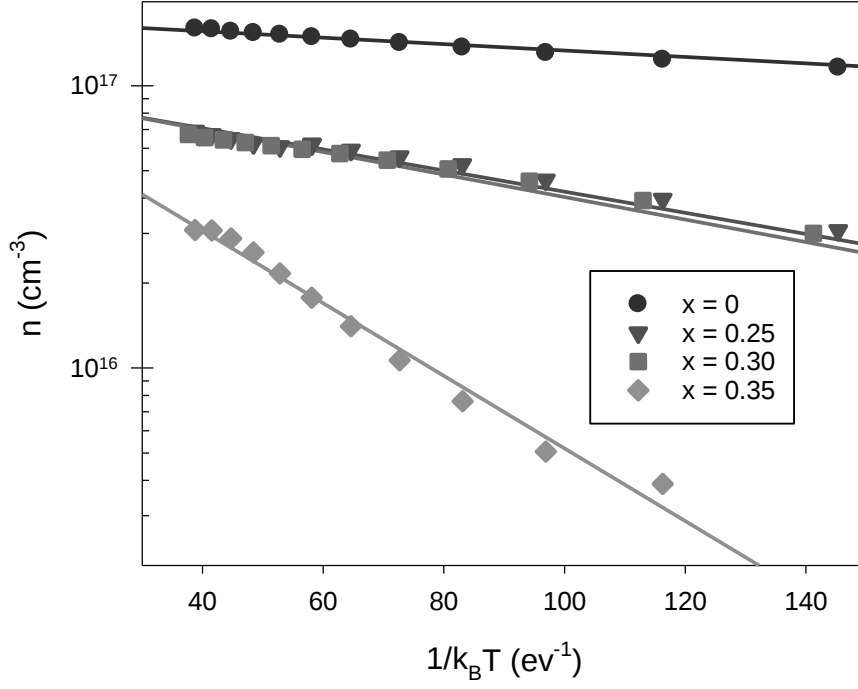


Figure 60. Temperature dependence of carrier concentration with I concentrations at $\sim 1.1 \pm 0.5 \times 10^{17} \text{ cm}^{-3}$ in CdTe and $\text{Cd}_{1-x}\text{Mg}_x\text{Te}$.

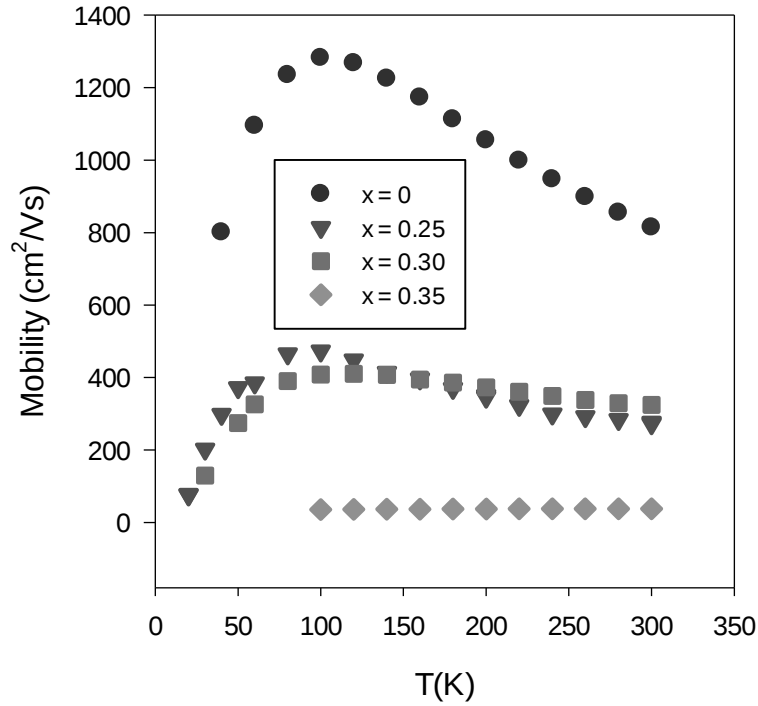


Figure 61. Temperature dependence of mobility with I concentrations at $\sim 1.1 \pm 0.5 \times 10^{17} \text{ cm}^{-3}$ in CdTe and $\text{Cd}_{1-x}\text{Mg}_x\text{Te}$.

Figure 60 further compares the activation energy of $\text{Cd}_{1-x}\text{Mg}_x\text{Te}$ as x ranges from 0 to 0.35. The activation energy of iodine in $\text{Cd}_{1-x}\text{Mg}_x\text{Te}$ was determined by fitting the data to the charge balance equation (shown as lines in Figure 60), and the resulting values are presented in Table 11. Activation energy increases with increasing x value. The current data suggests a small increase in activation energy with increasing x up to $x \sim 0.3$, roughly 2.3 meV for every 0.05 in x . Above this value of x , the activation energy increased dramatically. The phenomenon underlying the rapid change in electrical properties around $x \sim 0.35$ is not clear and cannot be determined from our limited sample set. Fischer et al.³² postulated the presence of a deep donor state for halogen doping, which is pushed into the band gap with increasing x . Their results indicated that a rapid decrease in activation occurs for Cl at $x \sim 0.15$ and for Br at $x \sim 0.25$ -0.30. While their data did not indicate a similar feature related to I for their samples with x estimated to be comparable to 0.35, there likely are differences between their x -determination and those in this study, and it is possible that the x -value used allows observation of this phenomenon for I.

Table 11. Activation energies of iodine in $\text{Cd}_{1-x}\text{Mg}_x\text{Te}$ at different Mg compositions.

Mg composition x in $\text{Cd}_{1-x}\text{Mg}_x\text{Te}$	E_a (meV)
0	6
0.25	17
0.30	20
0.35	58

The $\text{Cd}_{0.65}\text{Mg}_{0.35}\text{Te}$ sample with $n \sim 3 \times 10^{16} \text{ cm}^{-3}$ had an iodine concentration of $6 \times 10^{16} \text{ cm}^{-3}$, which implies that the free-carrier concentration of $3 \times 10^{16} \text{ cm}^{-3}$ at room temperature is consistent with the 58 meV activation energy and is not due to compensation. Little temperature dependence was observed for n-type carrier

concentration in CdMgTe at a doping concentration above $5 \times 10^{16} \text{ cm}^{-3}$. A similar observation was made in I-doped CdTe where little temperature dependence was observed for doping levels above $1 \times 10^{17} \text{ cm}^{-3}$. The mobility of iodine-doped $\text{Cd}_{1-x}\text{Mg}_x\text{Te}$, as shown in Figure 61, was observed to increase as the x value of Mg decreases.

PLI of the two iodine-doped DH samples, z-401 and z-403, are compared to PLI of undoped samples: z-400, z-371, z-373, and z-374. PLI of z-400 tends to be the lowest due to the high density of twin defects when compared to z-401 as shown in Figure 62. Similarly, z-371 has lower PLI compared to z-373 and 374 because it has more defect density than z-373 and z-374, but it has higher PLI compared to z-400 because it has less defect density than z-400. The cPL images of these samples, which show defects represented as dark spots, are shown in Figure 63. Generally, the PLI of these samples increases as doping increases, which is expected since higher doping will lead to stronger radiative recombination and eventually results in higher PL intensities. Also, PLI decreases as defect densities increase.

PLI of undoped DHs and I-doped DHs with various concentrations were studied as shown in Figure 64. The absorber-layer thickness of these DHs vary from $0.25 \text{ }\mu\text{m}$ to $2.5 \text{ }\mu\text{m}$ while the Mg x composition of the the barrier layers was kept at ~ 0.35 . All the DH samples have $1.5 \text{ }\mu\text{m}$ -thick buffer layer except sample z-360, which had $1 \text{ }\mu\text{m}$ -thick buffer layer. Samples z-360 to z-433 were grown on (100)-oriented InSb substrates, while z-436 and z-437 were grown on (100)-oriented CdTe substrates. As observed in the previous sample set, the PLI increases as doping increases, and samples grown on InSb substrates have higher PLI than samples grown on CdTe substrates. In addition, it was observed that PLI increases with absorber-layer thickness.

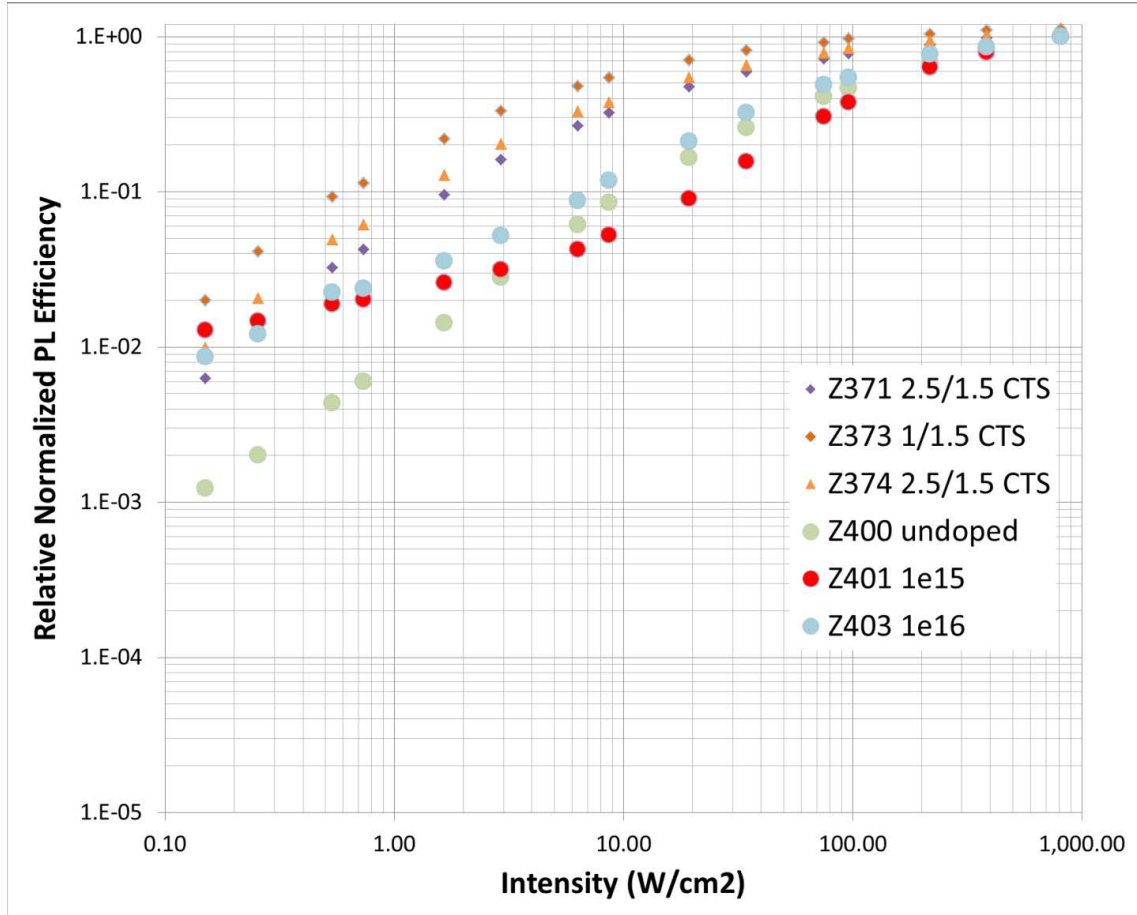


Figure 62. PLI of iodine-doped DH samples, z-401 (1.5 μm CdTeSe buffer, 2 μm absorber CdTeSe:I, I-doping of $1\text{E}15$) and z-403 (1.5 μm CdTeSe buffer, 2 μm absorber CdTeSe:I, Idoping of $1\text{E}16$), and four undoped samples, z-400 (1.5 μm CdTeSe buffer, 2 μm absorber CdTeSe, high-twin defect), z-371 (1.5 μm CdTeSe buffer, 2.5 μm absorber CdTeSe), z-373 (1.5 μm CdTeSe buffer, 2.5 μm absorber CdTeSe), and z-374 (1.5 μm CdTeSe buffer, 2.5 μm absorber CdTeSe).

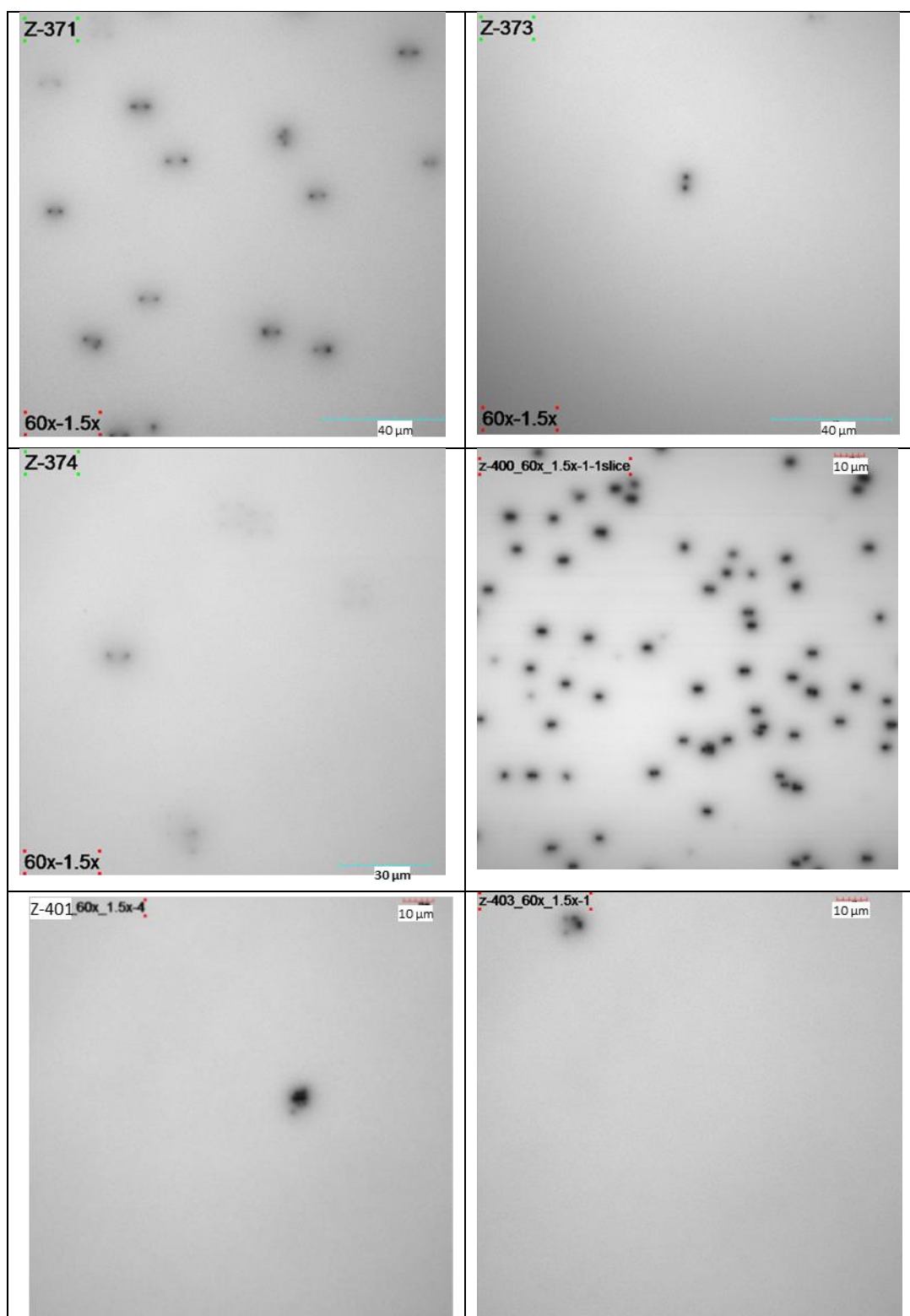


Figure 63. cPL images of z-371, z-373, z-374, z-400, z-401, and z-403.

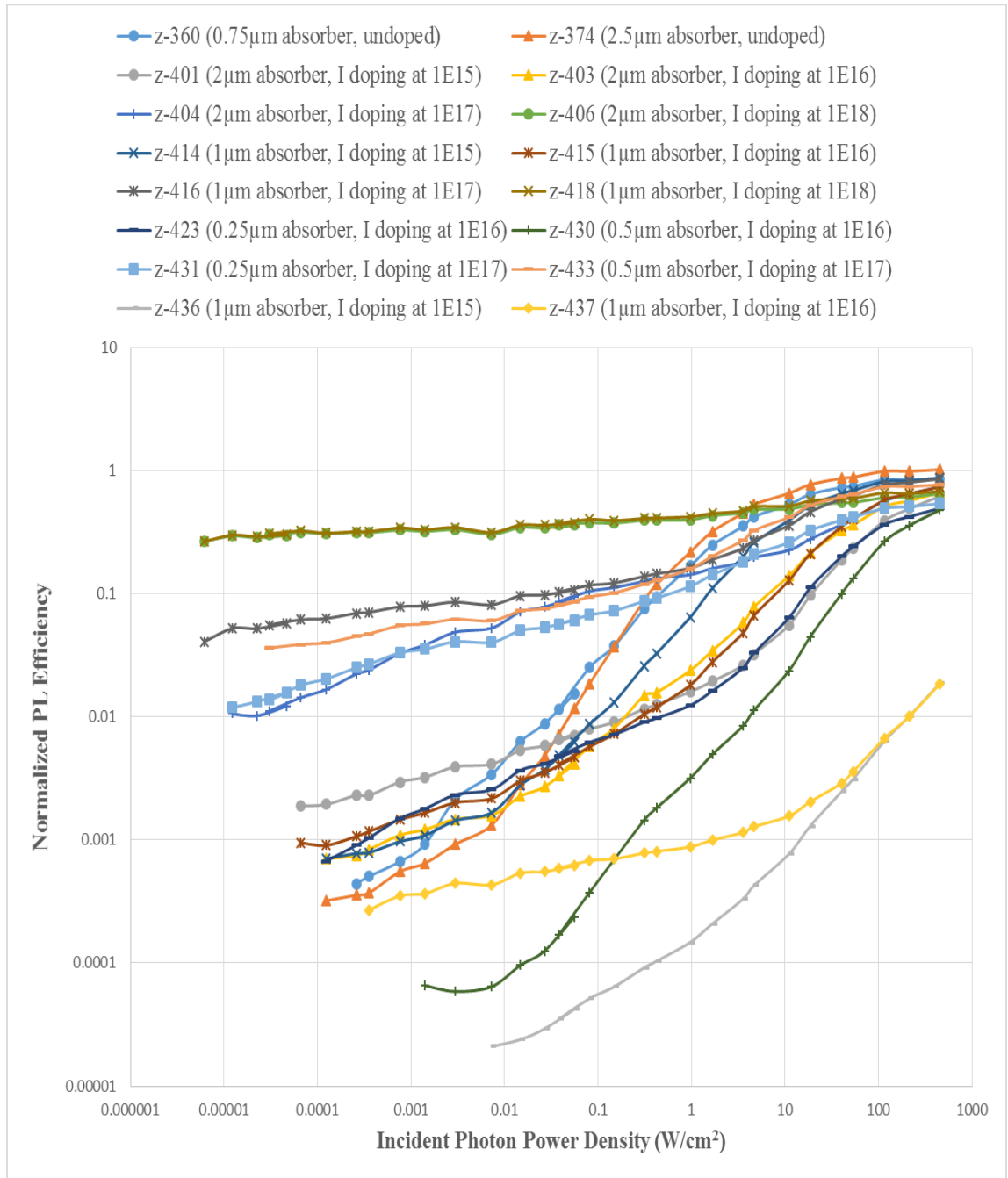


Figure 64. PLI of DH samples with various iodine concentration at various absorber layer thicknesses. Samples z-360 to z-433 were grown on (100)-oriented InSb substrates while z-436 and z-437 were grown on (100)-oriented CdTe substrate.

The impact of doping on carrier lifetime was studied using four DH samples doped with different iodine concentration. These samples have identical structures. The measured carrier lifetime in these samples is presented in Table 12.

Table 12. Concentration and lifetime of iodine-doped samples.

	Estimated doping concentration	Measured lifetime
z-402	1×10^{16}	750
z-404	1×10^{17}	91
z-406	1×10^{18}	10

For these I-doped DH samples, the appropriate low-injection TRPL lifetimes for the grown I-doped double heterostructures is given as

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_{rad}} + \frac{1}{\tau_{SRH}} + \frac{2S}{d} \quad (4.3)$$

where S is the surface recombination velocity and d is absorber thickness in the last term, which represents the effect of surface recombination. The radiative lifetime is given by

$$\tau_{rad} = \frac{1}{B_{rad}n\phi} \quad (4.4)$$

where n is the carrier concentration and B_{rad} is the radiative parameter. The parameter ϕ is the photon-recycling factor, which recognizes the rate that photons emitted in the radiative recombination process reabsorbs to create another electron hole pair, effectively recycling the original pair in high-quality materials, especially in a thick DH configuration. It is equal to the probability that a given radiative recombination event's photon is not absorbed to form a new pair.

Figure 65 contains a plot of the TRPL lifetimes measured for three iodine-doping levels at various absorber thicknesses in CdTe/Cd_{0.65}Mg_{0.35}Te DHs. As shown in section 3.4.2, this CdMgTe barrier composition resulted in a SRV of 160 cm/s with nominally undoped material grown. The gray line in the graph illustrates the expected upper limit on TRPL lifetime expected due to surface recombination based on this value. From the results for TRPL shown, it is clear that several values exceed this limit, suggesting that SRV in these doped samples is actually less than 160 cm/s. Assuming that the three highest values

for the $n \sim 1 \times 10^{16} \text{ cm}^{-3}$ DHs are due primarily to surface recombination and radiative recombination with $\phi \sim 1$, the measured lifetimes indicate a SRV of order 25 cm/s. The radiative lifetimes indicated for a given doping level assuming $\phi \sim 1$ and $B_{rad} = 1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ are shown and color-coded along with the TRPL measured for the associated doping levels. The $n \sim 1 \times 10^{16} \text{ cm}^{-3}$ DHs seem to be reasonably explained without invoking photon recycling. In contrast, the majority of the TRPL lifetimes measured for the $n \sim 1 \times 10^{17} \text{ cm}^{-3}$ and $n \sim 1 \times 10^{18} \text{ cm}^{-3}$ DHs exceed the radiative limit by factors of three to six, suggesting that recycling is a significant factor. This effect is consistent with what was observed for doped GaAs/AlGaAs DHs, emphasizing that, once surface recombination is controlled, the electronic properties of CdTe are comparable to those of GaAs, with the potential benefits of a slightly lower radiative recombination parameter.

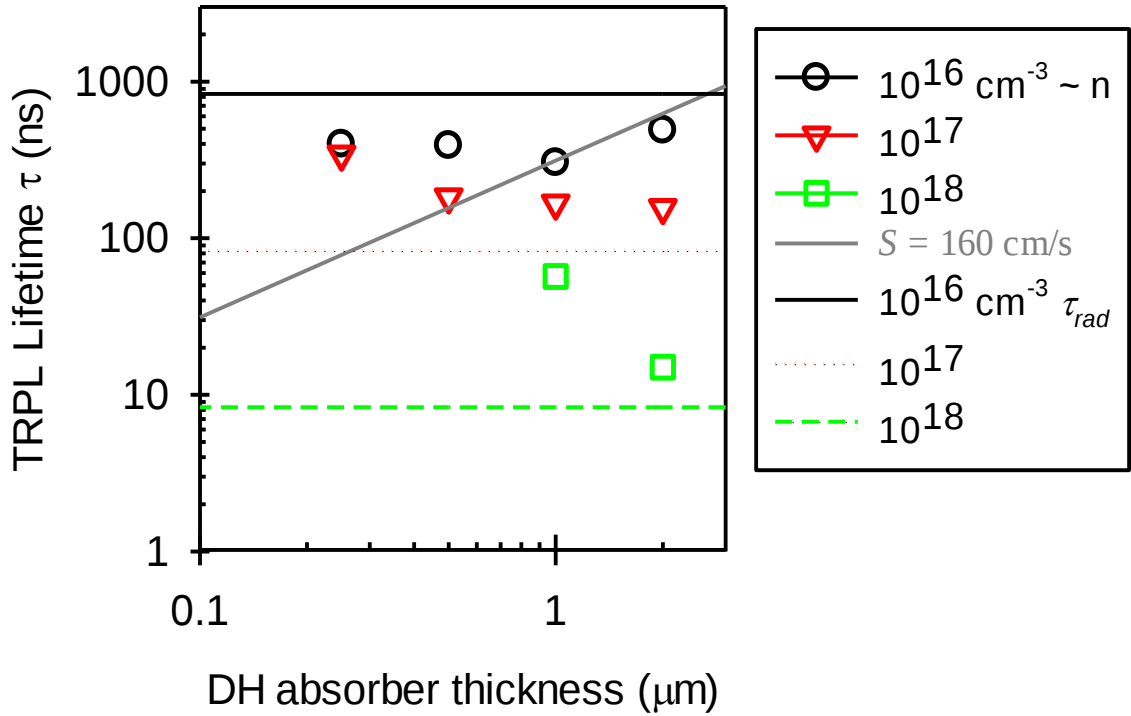


Figure 65. TRPL lifetimes measured for three doping concentrations at various absorber thicknesses in CdTe/Cd_{0.65}Mg_{0.35}Te DHs. Radiative lifetimes are shown, assuming photon recycling is not present, ($\phi \sim 1$) and $B_{rad} = 1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$.

These iodine-doped samples show long lifetimes with evidence of photon-recycling effects and no evidence of PL degradation with doping as high as $2 \times 10^{18} \text{ cm}^{-3}$ as shown in Figure 66, which is in contrast to In as it exhibits significant non-radiative recombination at levels above $5 \times 10^{16} \text{ cm}^{-3}$.²²

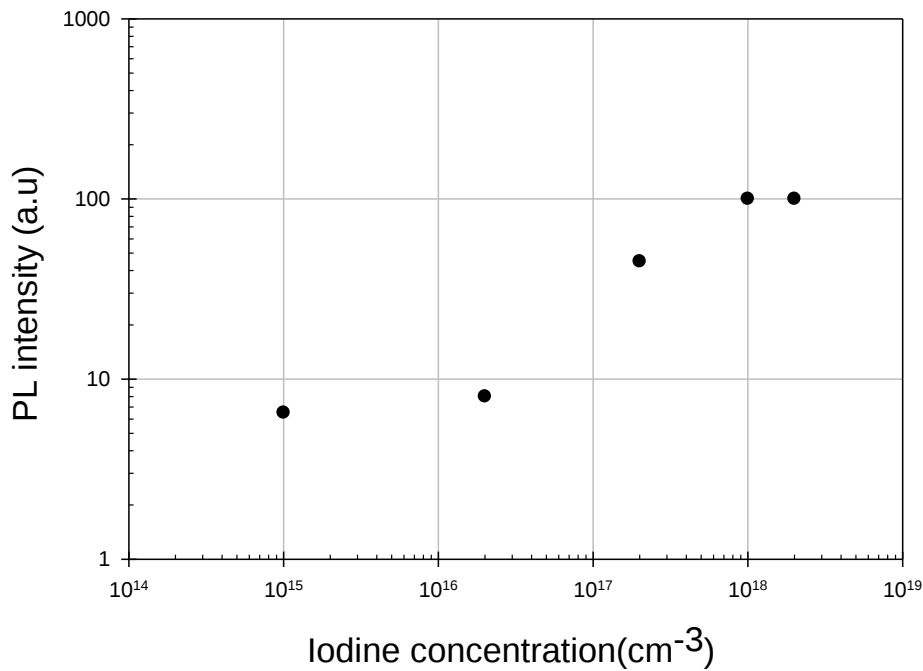


Figure 66. PL intensity vs. iodine concentration in iodine-doped CdTe/CdMgTe DHs at various doping concentrations.

4.3 CdTe:As

Group V elements have lower diffusivity as dopants in CdTe than group I elements because the size of group V atoms are larger than the size of group I atoms, hence they are more stable against thermally induced diffusion. This is particularly of interest in doping CdTe because of its low activation energy and stability. Cd_3As_2 , whose

vapor pressure is suitable for an MBE process, is used to achieve As doping in this project. The use of Zn_3As_2 compound source material to achieve As doping gave enhanced incorporation in ZnSe ,¹⁰⁹ and ZnTe .¹¹⁰ A similar result of As-incorporation enhancement is expected to be achieved with the use of Cd_3As_2 as the source material.

4.3.1 Experimental details

For this project, Cd_3As_2 was used as the source material to deliver arsenic flux for the purpose of achieving As doping in CdTe . The initial phase of the As-doping experiments as carried out using a standard effusion cells while the final phase of the As-doping experiments as performed using a valved corrosive source (VCOR) to crack As_4 to As_2 in order to see if it could resolve the issue of the solubility limit that was observed in the initial phase of the As-doping experiment.

VCOR 110 by Riber is a valved source designed with two heating zones—a reservoir for heating the bulk material and the tip for cracking—to achieve reproducible flux. The tip zone can operate at temperatures up to 900 °C while the reservoir can operate at temperatures up to 500 °C. The filaments used for heating in both zones are made of Ta wire, and the crucibles are made of pyrolytic boron nitride (PBN). The valve of this source is also made of PBN so that the vapor produced does not encounter any metal before the vapor leaves the source. The major external features, including power leads for the two zones, valve thimble, valve stem, thermocouple connectors, and the water cooling enclosure, are shown in Figure 67.

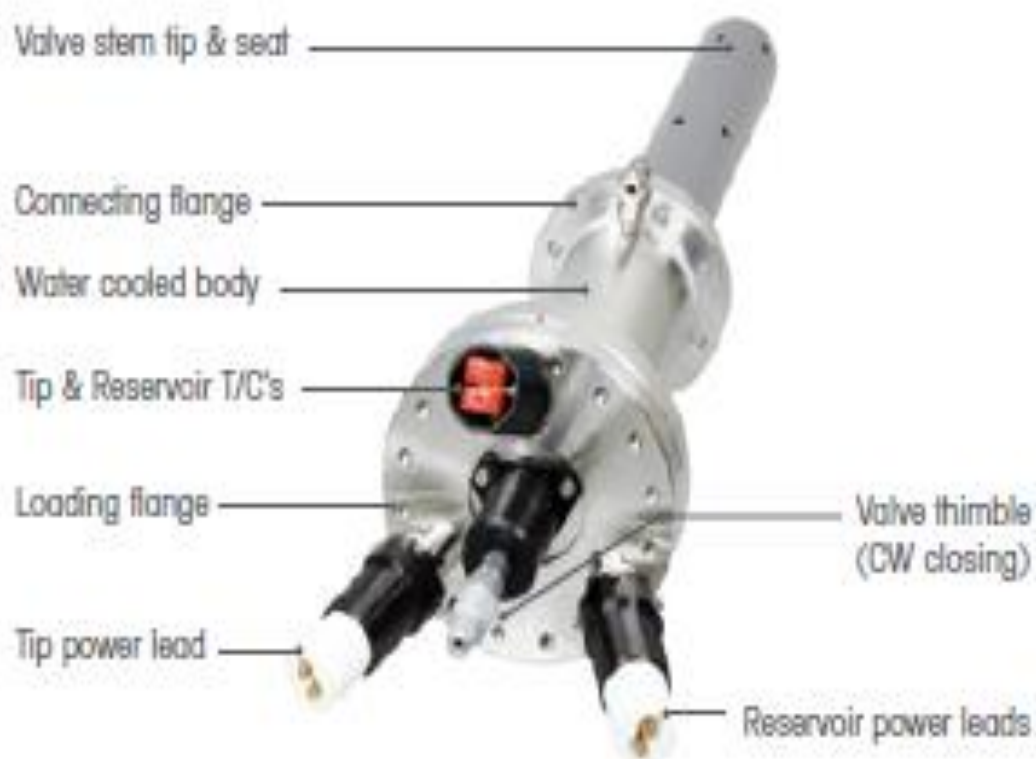


Figure 67. Typical VCOR showing its external features.

Garcia et al.¹¹¹ reported the use of a different catalyst in cracking As and concluded that rhenium has the highest cracking efficiency among these materials with the exception of Pt, which is reactive with As at temperatures above 500 °C. Rhenium achieved conversion efficiencies of 95% and 50% at about 700 °C and 575 °C, respectively, as shown in Figure 68.¹¹¹

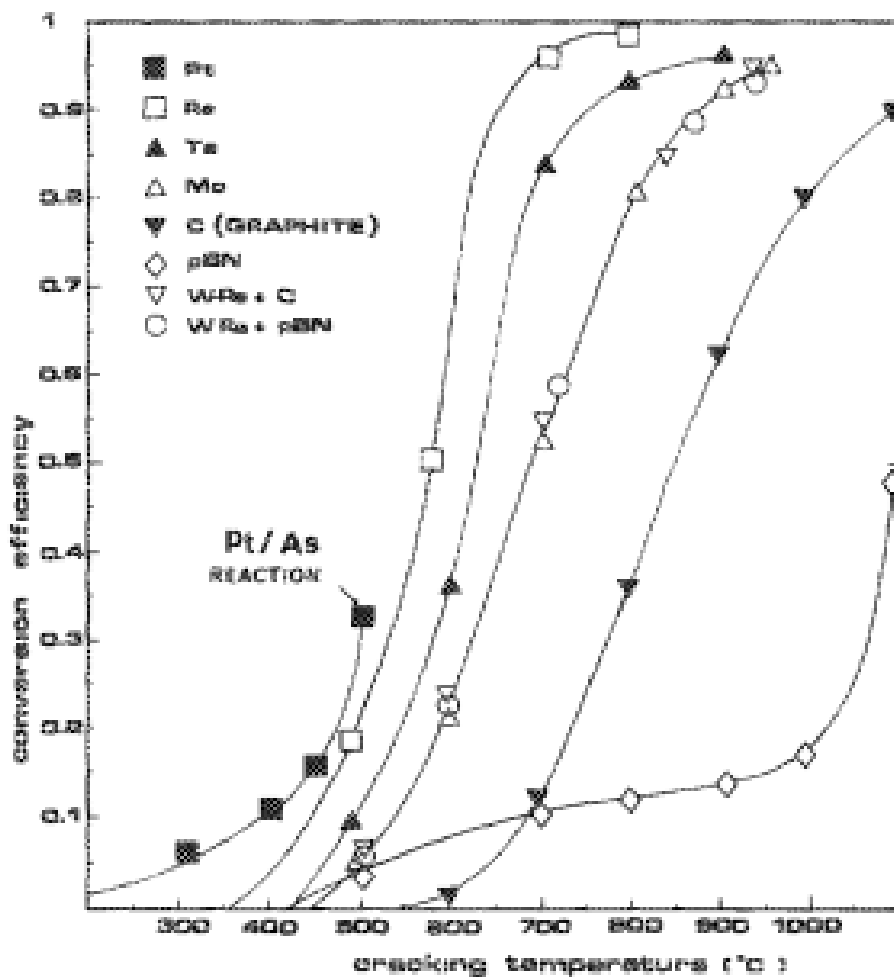


Figure 68. As₄ cracking efficiency as a function of cracker temperature using Pt (■), Re (□), Ta (▲), Mo (△), Graphite (▼), PBN (◇), W-Re+C (▽), and W-Re+pBN (○) catalysts.¹¹¹

In order to achieve efficient cracking of As₄, a cracker insert was built with PBN rods, Ta foil and rhenium (Re) wire. The rhenium wire used in building the cracker insert has an assay percent range of 99.7% and is 0.5 mm in diameter, and it was purchased from Fisher Scientific. The cracker insert was designed by wrapping the rhenium wire around the inner Ta foil as shown in Figure 69. The insert was then placed in the hot zone of the VCOR 110 used in this project was modified with an insert that was placed in the hot zone of a rhenium (Re) wire to achieve more efficient catalytic cracking in As.

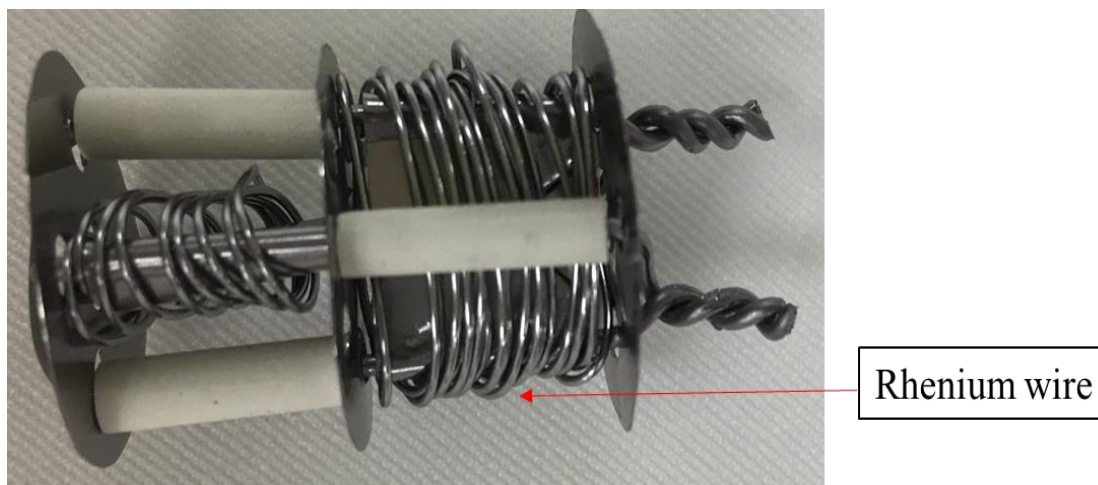


Figure 69. VCOR cracker insert built with rhenium wire to achieve high-efficiency cracking of As_4 .

CdTe (100), CdZnTe (100), and InSb (100) substrates were used in growing the As-doped samples. As-doped samples grown for the purpose of Hall measurements were limited to semi-insulating CdTe and CdZnTe substrates. The growth of these Hall measured samples usually start with a 100 nm buffer layer and is then followed by the As-doped layers. All As-doped samples were grown under Cd-rich conditions to maintain stoichiometric condition. In addition to the Cd overpressure as a measure for defect control, some samples were grown with Zn incorporation. For these samples, ZnTe and CdTe alloying was used for As-doping incorporation since stronger bonds in CdZnTe than CdTe will lead to less defect formation in CdZnTe ,¹¹² hence compensation is expected to be less in CdZnTe than CdTe . Approximately 4% Zn incorporation was used in the CdZnTe:As for the purpose of this As incorporation enhancement in order to lattice match the available $\text{Cd}_{0.96}\text{Zn}_{0.04}\text{Te}$ substrates used for these samples.

During the initial phase of these As-doped experiments, several As-doped samples were grown for the purpose of dopant incorporation calibration, SIMS analysis, Hall measurement, and diffusion studies. The stepped calibration samples were grown to calibrate dopant concentration as a function of either temperature or flux ratio. These samples were grown with undoped CdTe spacers in between doped layers. These spacers were 200-nm thick in most cases and were intended to differentiate doping incorporation at each given temperature. These CdTe spacers were also used in other samples where one or more growth parameters were varied in a particular sample so as to differentiate between each doping incorporation.

Despite efforts to promote As atoms on Te lattice sites during growth, the majority of the As atoms in as-grown CdTe based samples may not be substituted on Te sites since the As incorporation was not electrically active at room temperature. Atoms that are not occupying lattice sites may require thermal treatment step known as activation anneal to move dopants onto lattice sites. Activation annealing is required to tackle the issue of the low activation of As in as-grown CdTe based samples. After growth, samples were annealed ex-situ from the MBE system in a sealed ampoule under Cd overpressure to keep the surface Cd rich during activation annealing or in a rapid thermal annealing systems without Cd overpressure. These anneals were done from 400 °C and above. After annealing, characterization techniques were used to study the effects of thermal annealing and rapid thermal processing on doping.

Dopant incorporation for the As-doped CdTe-based samples in this project were calibrated with secondary ion mass spectroscopy (SIMS), which was done at EAG Laboratories, while carrier concentration was measured by the C-V technique or the van

der Pauw Hall effect technique using either indium soldered contacts or MBE-grown p-type PbTe contacts. The results from these characterized As-doped samples are discussed in the next section.

4.3.2 Results

4.3.2.1 Arsenic doping using standard effusion cell

Calibration samples were grown on InSb, CdTe, and CdZnTe substrates with various growth conditions, and the effects of the growth parameters—growth temperature, Cd overpressure, a Cd₃As₂/CdTe flux ratio, and Zn incorporation—on As-doping incorporation were studied. The results were analyzed to determine controllability and effectiveness of As doping in CdTe using Cd₃As₂ supplied from a standard effusion cell.

4.3.2.1.1 Growth temperature studies

Calibration samples z-369 and z-370 were grown to investigate control over As incorporation and to give an initial determination of the dependence of As incorporation on a Cd₃As₂/CdTe flux ratio. Sample z-369 was grown at 234 °C, and sample z-370 was grown at 244 °C while varying the Cd₃As₂/CdTe flux ratio. In both samples, CdTe was about $7.3 \pm 0.5 \times 10^{-7}$ Torr while Cd flux was about 1.5×10^{-7} Torr. For sample z-369, the Cd₃As₂/CdTe flux ratio was varied as 0.1, 0.3, 0.5, 0.7, and 0.9 while for sample, the z370 Cd₃As₂/CdTe flux ratio was varied as 0.25, 0.4, 0.6, 0.9, and 1.2. SIMS measurements gave the As concentration for each doping profile as shown in Figure 70.

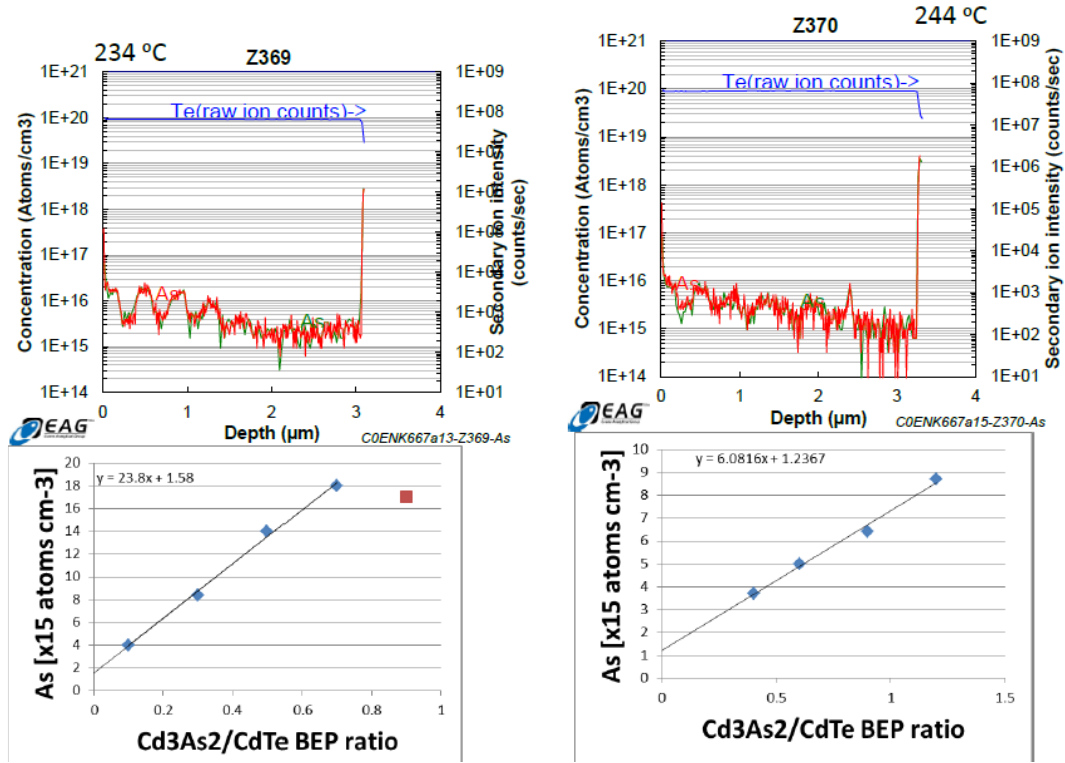


Figure 70. SIMS profile of two As-doped CdTe samples grown on InSb (100) at different temperatures with varying Cd₃As₂/CdTe flux, and the linear relationship between incorporated As atoms and the Cd₃As₂/CdTe flux ratio.

A maximum As concentration of approximately 10^{16} atoms/cm³ was achieved in these samples according to the SIMS profile in Figure 70. Also shown in Figure 70 is a linear relationship between incorporated As atoms and the Cd₃As₂/CdTe flux ratio. Assuming that other growth conditions are relatively similar at an Cd₃As₂/CdTe flux ratio of 0.9, with the exception of the substrate temperature, it is clear that z-369 has more atoms incorporated, which suggests higher arsenic incorporation at lower temperatures.

The effect of substrate temperature on As incorporation was further examined in z-389. In this sample, substrate temperature was varied at 234 °C, 215 °C, 195 °C, and 176 °C while the Cd₃As₂/CdTe flux ratio was fixed as 1.0. A CdTe flux of about 6×10^{-7} Torr and a Cd flux of about 1.3×10^{-7} Torr was used for the growth. Observation of the

SIMS profile of sample z-389 grown on InSb (100) as shown in Figure 71(a) and sample z-454 grown on CdTe (100), as shown in Figure 71(b) suggests a strong dependence of As incorporation on temperature. The doping concentration of low 10^{16} atoms/cm³ at substrate temperature 234 °C measured in sample z-389 is comparable to the results achieved in sample z-369, indicating this result was reproducible for growth on InSb substrate. The rapid increase in As incorporation observed for the doping profile at low temperature was unexpected and accompanied by significant structural degradation. This rapid and tremendous As incorporation observed at ~175 °C in z-389 and z-454 appears to mark the onset of As segregation, which leads to surface accumulation. One interpretation is that at sufficiently low temperatures, defects are generated due to fast nucleation. These defects can act as nucleation sites, which will likely capture As atoms and lead to precipitation. Alternatively, As precipitation may lead to structural degradation. Afterwards, most structures were grown at temperatures above 200 °C.

The identical As concentration at 234 °C in z-369 and z-389 for similar Cd₃As₂/CdTe BEP ratio validates the temperature calibration experiment used to determine real temperatures for structures grown on InSb substrates. Sample z-454 grown on CdTe was initially designed to have real temperatures that are similar to sample z-389 grown on InSb so that As incorporation using these substrates can be compared. The unexpected rapid increase of As incorporation seen in SIMS results of z-454 grown on CdTe substrate suggested that the temperature calibration used to determine the target temperatures for this sample may be off. The mistake in temperature calibration was later corrected to reflect the real growth as indicated in Figure 71 (b). The rapid increase of about three orders of magnitude from high 10^{17} atoms/cm³ nearly 10^{21} atoms/cm³ in z-

454 indicate that almost all the As atoms are sticking which suggest that the growth temperatures in this sample is lower than the growth temperatures in z-369. Z-454 have similar As incorporation with z-389 at ~175 °C.

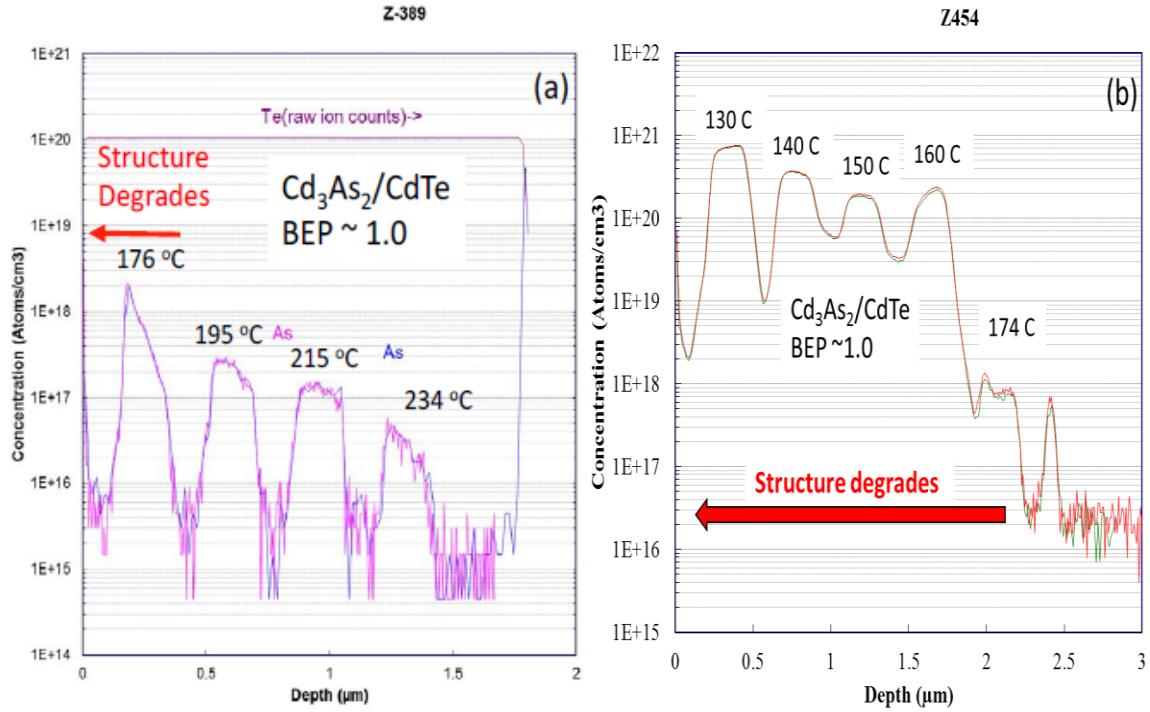


Figure 71. SIMS profile showing the effect of changing growth temperature in As-doped CdTe structures grown on (a) InSb (100) substrates and (b) CdTe (100) substrates.

4.3.2.1.2 Flux ratio studies - Cd₃As₂/CdTe BEP ratio and Cd overpressure

The effect of changing the Cd₃As₂/CdTe BEP ratio (the ratio varied as 0.5, 1.0, and 1.5) at a fixed substrate temperature of 205 °C was again studied in sample z-399 by growth, and the condition was analyzed using SIMS as shown in Figure 72. The SIMS profile showed a rapid increase in As incorporation for the Cd₃As₂/CdTe BEP ratio of 1.0 and 1.5 suggest that structures degrade significantly when a substrate temperature is low and As concentration is high. The doping concentration of $\sim 3 \times 10^{17}$ atoms/cm³ with a substrate temperature of 205 °C and a Cd₃As₂/CdTe BEP ratio ~ 0.5 in sample z-399 is

comparable with the doping concentration of $\sim 1 \times 10^{17}$ atoms/cm³ with a substrate temperature of 215 °C and a Cd₃As₂/CdTe BEP ratio ~ 1.0 in sample z-389. Although samples z-389 and z-399 show an As-dopant concentration of 10^{17} atoms/cm³, the structural degradation observed in these samples suggests that the As solubility limit in CdTe can be reached when the growth conditions of a substrate temperature below 200 °C and a Cd₃As₂/CdTe BEP ratio above 1.0 are applied together.

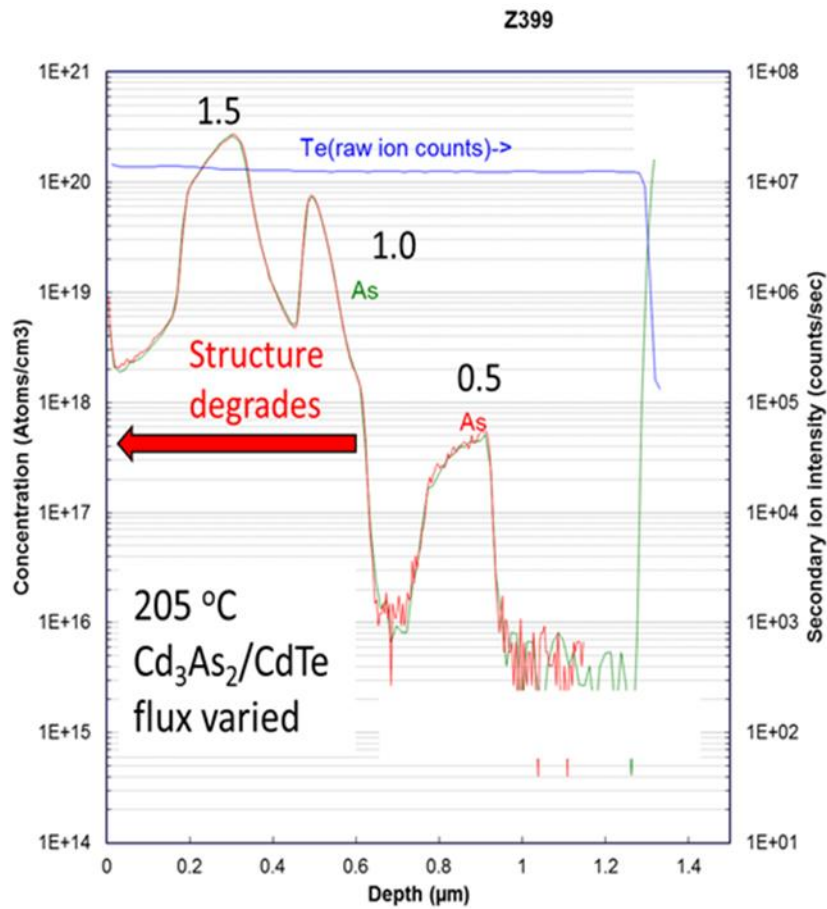


Figure 72. SIMS profile showing the effect of varying Cd₃As₂/CdTe BEP ratio in As-doped CdTe structure grown on InSb (100) substrate at 205 °C substrate temperature.

The effect of Cd overpressure was studied in sample z-466 where the CdTe flux was set at $\sim 8 \times 10^{-7}$ Torr and the Cd₃As₂/CdTe BEP ratio was fixed at 0.25. Growth

temperature and Cd overpressure were varied in different layers as shown in Figure 73. The target growth appear to be off, based on the other SIMS results. It was hard to correlate this SIMS result with other SIMS results but this result suggests that using 20% to 30% Cd overpressure at higher temperatures during As incorporation will likely not cause the structure to degrade.

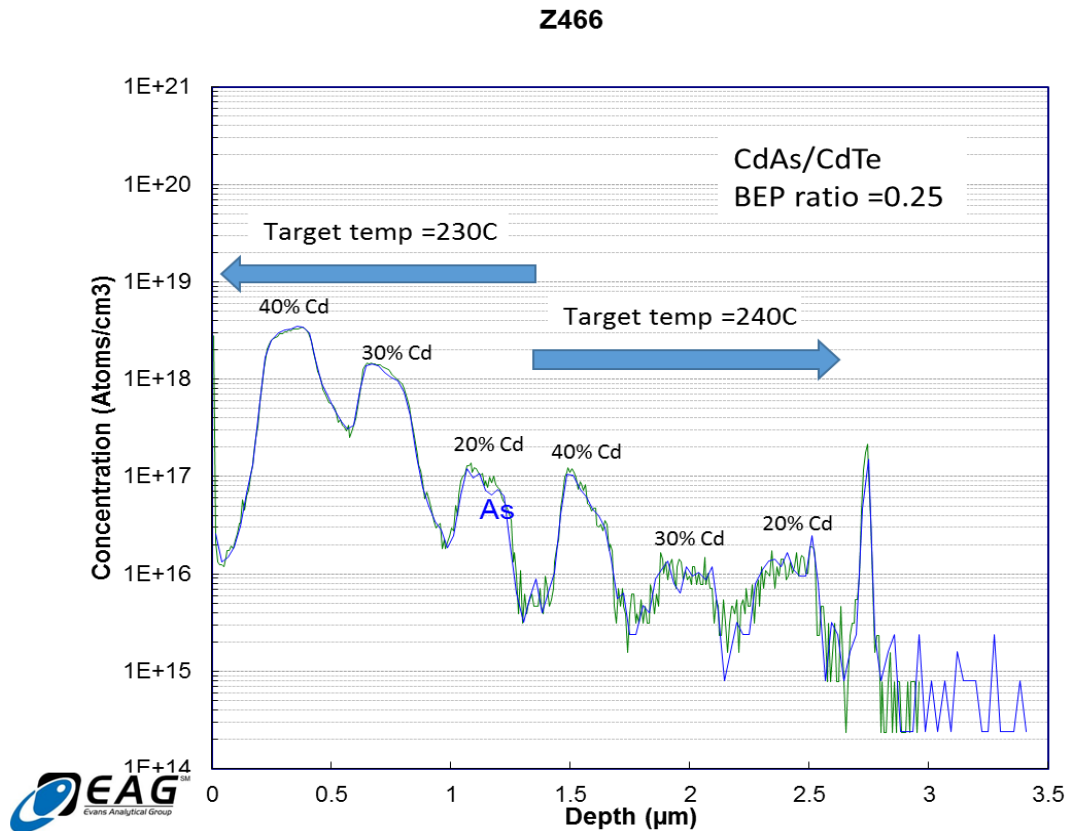


Figure 73. SIMS profile showing the effect of varying Cd/CdTe BEP ratio in As-doped CdTe structure grown on CdTe (100) substrate with Cd₃As₂/CdTe BEP ratio of 0.25 at target temperature of 230 °C and 240 °C.

Observation of a rapid and significant increase in As incorporation, as seen in samples like z-389 (Figure 71(a)), z-399 (Figure 72), z-454 (Figure 71 (b)), and z-466 (Figure 73) when As incorporation exceeds mid 10^{17} atoms/cm³, suggests that As dopants at this level may start to incorporate as precipitates, and the structure starts to degrade as

result of defect generation. The most significant observation in these As-doped samples is the rapid increase in As concentration accompanied by structure degradation as seen in samples z-399 (Figure 72), z-454 (Figure 71(b)), and z-466 (Figure 73). It is assumed that this rapid increase in incorporation is a result of As incorporating in the form of clusters or nanoscale precipitates rather than incorporating at substitutional sites. The speculation is that As is accumulating on the growing surface of the sample and, at some critical density, nucleates the As precipitation. This rapid increase starting at the onset of structural degradation suggests that the degraded structure captures much more As atoms than the un-degraded structure where As atoms are incorporated in the crystal lattice.

4.3.2.1.3 Solubility limit studies

Techniques like TEM and APT can be used to determine the presence of precipitates in doped semiconductors. Precipitates of dopants can be utilized to predict the solubility limit in the host semiconductor. It has been suggested that the solubility limit depends on growth conditions, making it difficult to establish a certain limit for a dopant element in a host semiconductor without considering the specific growth condition.

The effect of the rapid incorporation observed in some As-doped CdTe structures grown on both InSb (100), like sample z-399 (Figure 72), and CdTe (100), like samples z-454 (Figure 71 (b)) and z-466 (Figure 73), substrates is believed to be related to the As solubility limit in CdTe under the standard growth conditions used during the first part of this project.

APT work done at the Colorado School of Mines by Dr. Gorman's group was used to study the dopant distribution for different As incorporation levels in order to further investigate the As solubility limit in CdTe. The specimen from z-399 was investigated with APT. From the APT reconstruction shown in Figure 74 (a), As clusters were visibly observed in the region of the first 500-nm from the top surface where the sample was observed to be structurally degraded according to the SIMS profile in Figure 72. Whereas clustering of As was less visible in the region of 500-nm to 900-nm from the top surface where SIMS profile did not show significant structural degradation. For this APT specimen in sample z-399, the experimental As' nearest-neighbor distribution was compared to the random As distribution in order to analyze the extent of As enrichment and its preference for its nearest neighbor. This was done for two regions (covering the distance after 350 nm to 450 nm from the top surface and after 450 nm to 900 nm from the top surface) in this APT specimen as shown in Figures 74 (b) and 74 (c), respectively. Visual observation suggests that the region covering the distance after 350 nm to 450 nm from the top surface seems to show some degree of deviation from randomness. This observation is consistent with the visibility of As clusters in the APT image and the structural degradation observed in the SIMS result in Figure 72. The bimodal nature of nearest neighbor distribution of the region covering the distance after 350 nm to 450 nm from the top surface seems to indicate presence of As clusters. The experimental curve peak closer to the graph origin indicate that substantial amount of As atoms are in close vicinity to other As atoms. Whereas the experimental curve for the region covering the distance after 450 nm to 900 nm from the top surface seems to slightly follow the random distribution, indicating that As is fairly dispersed in

CdTe for this region. Again, this observation is consistent with the APT reconstruction and the SIMS result in Figure 72. The analysis of the nearest neighbor-distribution and random distribution suggests that As tends to preferentially segregate.

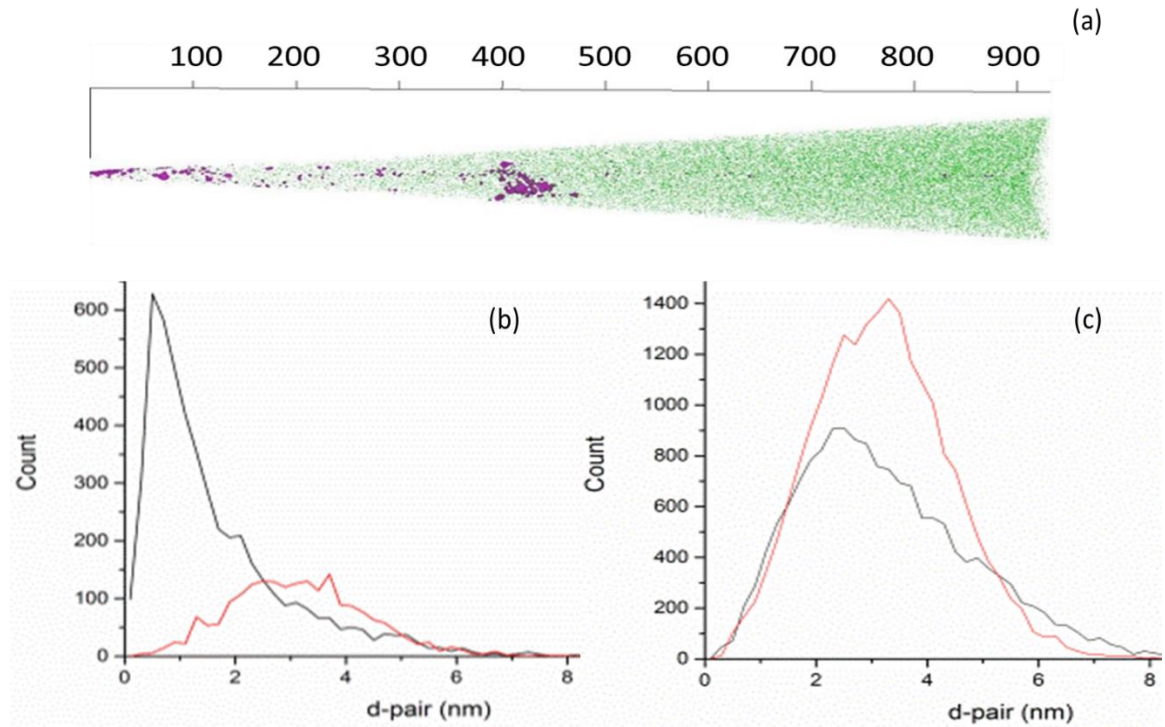


Figure 74. As concentration profile and nearest-neighbor distribution of an APT specimen prepared from sample z-399 by Colorado School of Mines. (a) APT reconstruction of this specimen with As represented as purple grains and Te represented as green grains, (b) experimental arsenic nearest-neighbor distribution in black and a random distribution in red from a region covering the distance after 350 nm to 450 nm from the top surface, and (c) a region covering the distance after 450 nm to 900 nm from the top surface.

Also, an APT reconstruction (shown in Figure 75 (a)) with the time of flight SIMS (shown in Figure 75 (c)) of As-doped CdTe with As concentration of 5×10^{17} atoms/cm³ was analyzed. Visual observation of the APT reconstruction suggests the absence of significant As clustering but the time of flight SIMS could not detect As

clustering, which detects clusters on the order of a few microns. This results suggest that the As clusters that may exist at this As concentration are on the nanoscale. The comparison of the experimental As' experimental nearest-neighbor distribution to the random distribution for this APT specimen shown in Figure 75 (b) does indicate some degree of deviation from randomness, which is consistent with the APT reconstruction and the time of flight SIMS results, also suggesting that As has preference for itself at this concentration.

For all the growth conditions investigated up to this point, it was observed that As incorporation above $7\text{-}8 \times 10^{17} \text{ cm}^{-3}$ definitely leads to structural degradation due to second-phase formation. Results from SIMS and APT studies suggest that As clusters will most likely be absent when the As incorporation level does not exceed $5 \times 10^{17} \text{ atoms/cm}^3$ but may become present once the As incorporation level exceeds $\sim 7.5 \times 10^{17} \text{ cm}^{-3}$. These results suggest that the As solubility limit in CdTe is around mid- 10^{17} cm^{-3} .

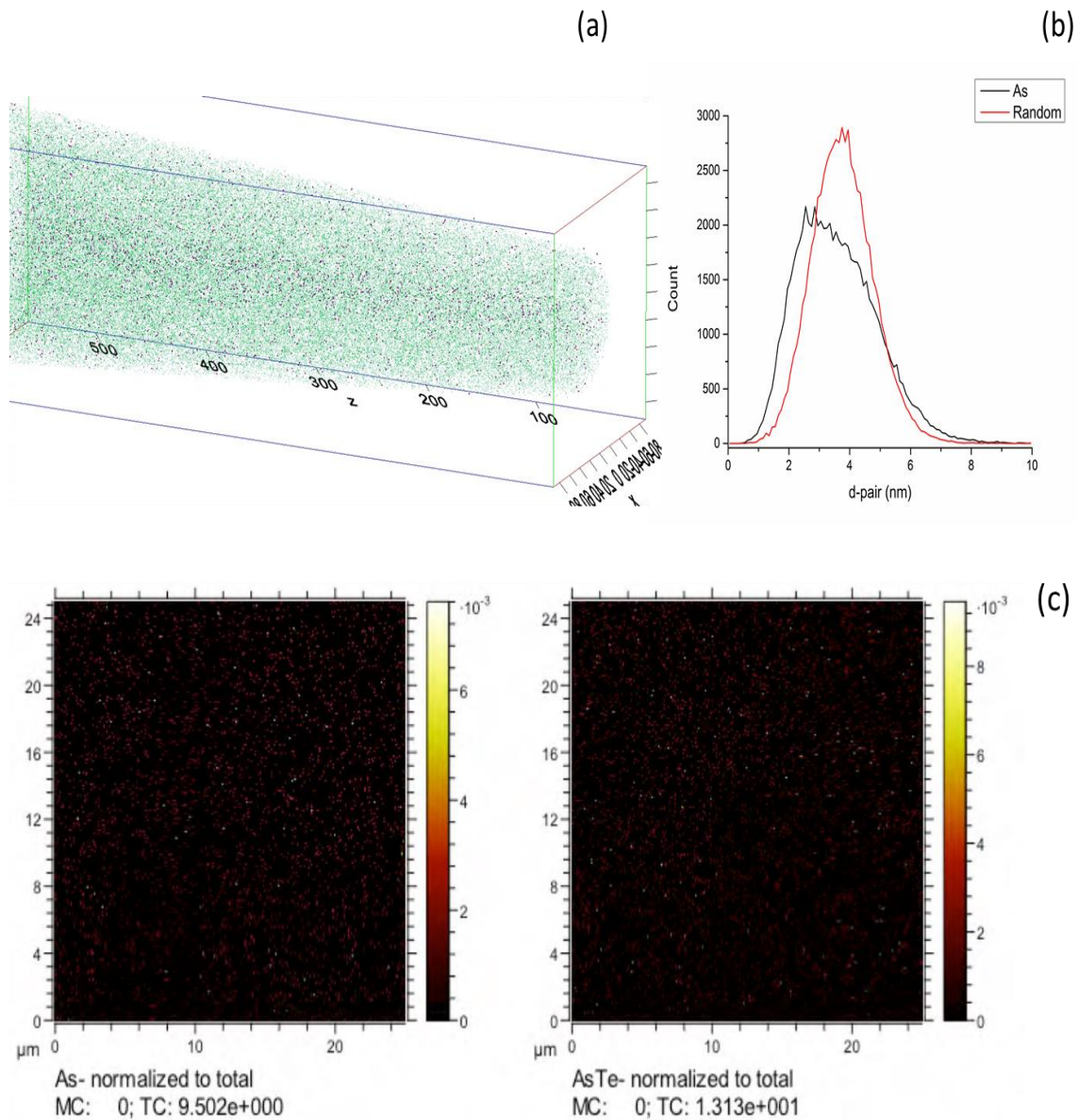


Figure 75. (a) APT reconstruction of a specimen with As concentration of 5×10^{17} atoms/cm³ (As is shown in purple with Te in green). (b) Experimental arsenic nearest-neighbor distribution in black, and a random distribution in red. (c) Time of flight SIMS maps of As and AsTe concentration.

4.3.2.1.4 Zn incorporation studies

A-center formation is possible in As-doped CdTe, but its formation is not likely in As-doped ZnTe,¹¹³ providing a chance that A-centers may be suppressed in CdZnTe. Based on this, the effect of Zn on As incorporation using Cd_{0.96}Zn_{0.04}Te (100) substrates was studied. Most of the As-doped samples grown to this point were done with CdTe and InSb substrates. For this sample, ~4% Zn was used to achieve a near-lattice-match condition and to investigate if Zn can enhance As incorporation. Growth temperature was fixed at ~240 °C, and Cd overpressure was fixed at 30% while the Cd₃As₂/CdTe ratio was varied. Incorporation of arsenic increases linearly with the Cd₃As₂/CdTe BEP ratio as shown in Figure 76. The linear relationship is showing As concentration of $\sim 5 \times 10^{15} \text{ cm}^{-3}$ when the Cd₃As₂/CdTe BEP ratio is zero suggest that there was background As in the MBE system prior to the sample growth. The SIMS measurement shows a step-like profile throughout the sample, indicating a uniform distribution of As atoms, which has been difficult to achieve in previous As-doped samples. The SIMS profile (shown in Figure 76) shows that the layer doped with a Cd₃As₂/CdTe ratio of 3:1 has the highest As incorporation, but the SIMS profile of the Cd₃As₂/CdTe ratio of 2:1 and 1:1 shows a slightly better step-like profile than the profile of 3:1, which suggests that doping using an Cd₃As₂/CdTe ratio of 2:1 or 1:1 might give slightly better uniform doping than a ratio 3:1. The SIMS profile of Cd₃As₂/CdTe ratio of 1:1 showing As incorporation of $\sim 2 \times 10^{16} \text{ cm}^{-3}$ is consistent with the SIMS profiles of z-369 (Figure 70) and z-389 (Figure 71(a)) with similar temperatures. It is noted that doping concentration and uniformity depend on other factors, too. The lack of evidence of rapid increase in As incorporation z-496 suggests that the high substrate may be needed in controlling As incorporation. The evidence of near-flat SIMS profile in this sample compared to z-369

and z-389 suggest that Zn incorporation may likely assist uniform As incorporation at high temperature.

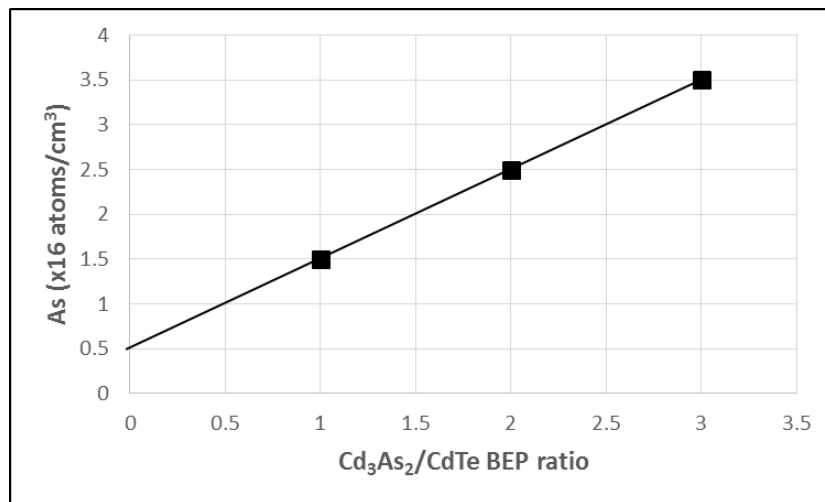
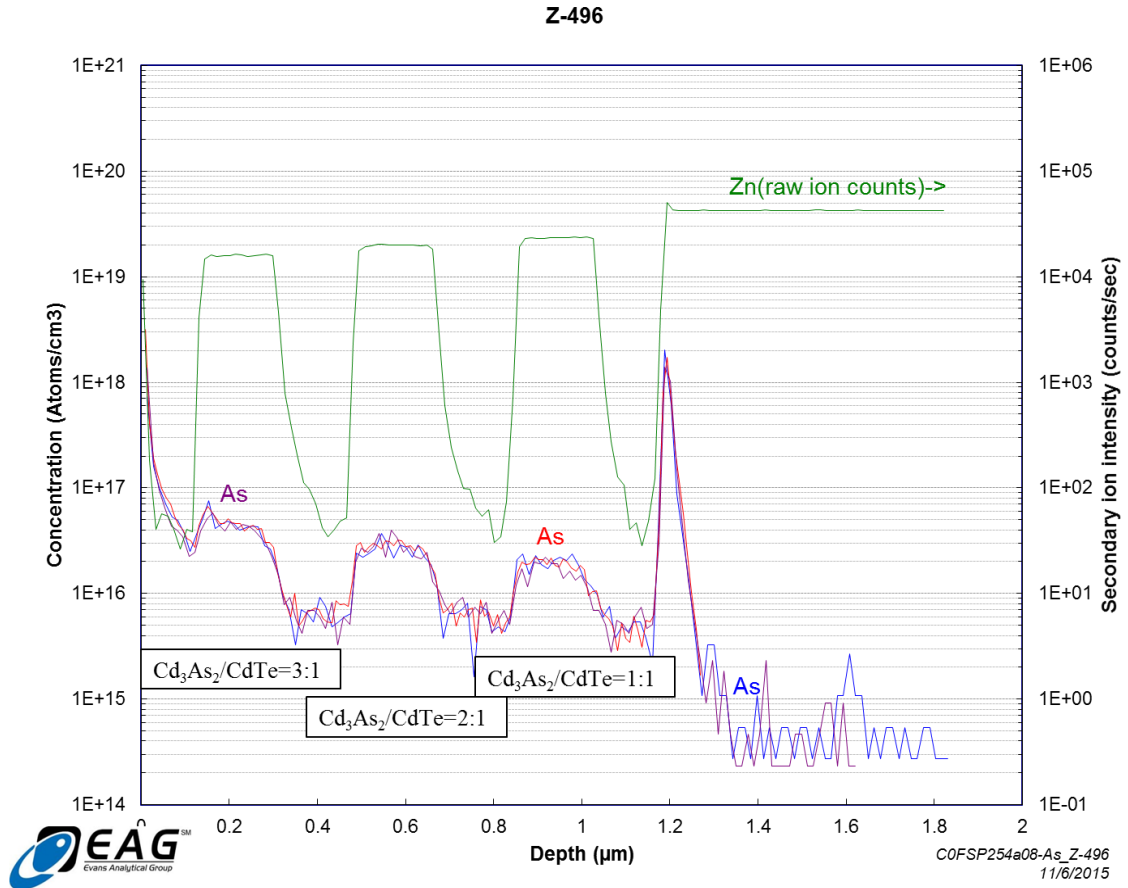


Figure. 76. SIMS profile of As-doped $\text{Cd}_{0.96}\text{Zn}_{0.04}\text{Te}$ sample grown on $\text{Cd}_{0.96}\text{Zn}_{0.04}\text{Te}$ (100) substrate with varying $\text{Cd}_3\text{As}_2/\text{CdTe}$ BEP ratio, and the linear relationship between incorporated As atoms and the $\text{Cd}_3\text{As}_2/\text{CdTe}$ BEP ratio.

Although As incorporation from Cd_3As_2 using an effusion cell can now be reasonably controlled, SIMS-measured As incorporation is still in the low 10^{16} cm^{-3} despite efforts to achieve 10^{17} cm^{-3} As incorporation without reaching the solubility limits. Although carrier concentration of 10^{16} cm^{-3} was achieved, it was somewhat challenging to reproduce 10^{16} cm^{-3} -carrier concentration. It is assumed that reproducible, uniform doping at high As incorporation without reaching the solubility is needed to improve on the carrier concentration and the doping efficiency, hence the need for cracking As_4 .

4.3.2.2 Arsenic doping using cracker source

A VCOR cracker source, described in section 4.3.1, was installed to improve on the results achieved during the initial phase of As-doping experiment for this research project. The main goal of the final phase was to combine optimal growth conditions obtained in the initial phase with As_4 cracking, which was meant to improve the sticking rate of As atoms in order to achieve efficient doping.

To study the effect of temperature using this new source, three samples (z-553, z-554, and z-555) were grown on CdTe (100) substrates at 250 °C, 240 °C, and 230 °C, respectively, while other growth parameters, such as a $\text{Cd}_3\text{As}_2/\text{CdTe}$ BEP ratio of ~ 1.0 and a Cd/CdTe BEP ratio ~ 0.3 , were kept constant. The SIMS profile of these samples are presented in Figure 77. These results show a uniform distribution of As atoms. Also, this result show that As can be reproducibly doped at high temperatures since the As

dopant concentration, which is $\sim 4 \times 10^{16}$ atoms/cm³, in these samples did not change significantly within the 230 °C to 250 °C temperature range.

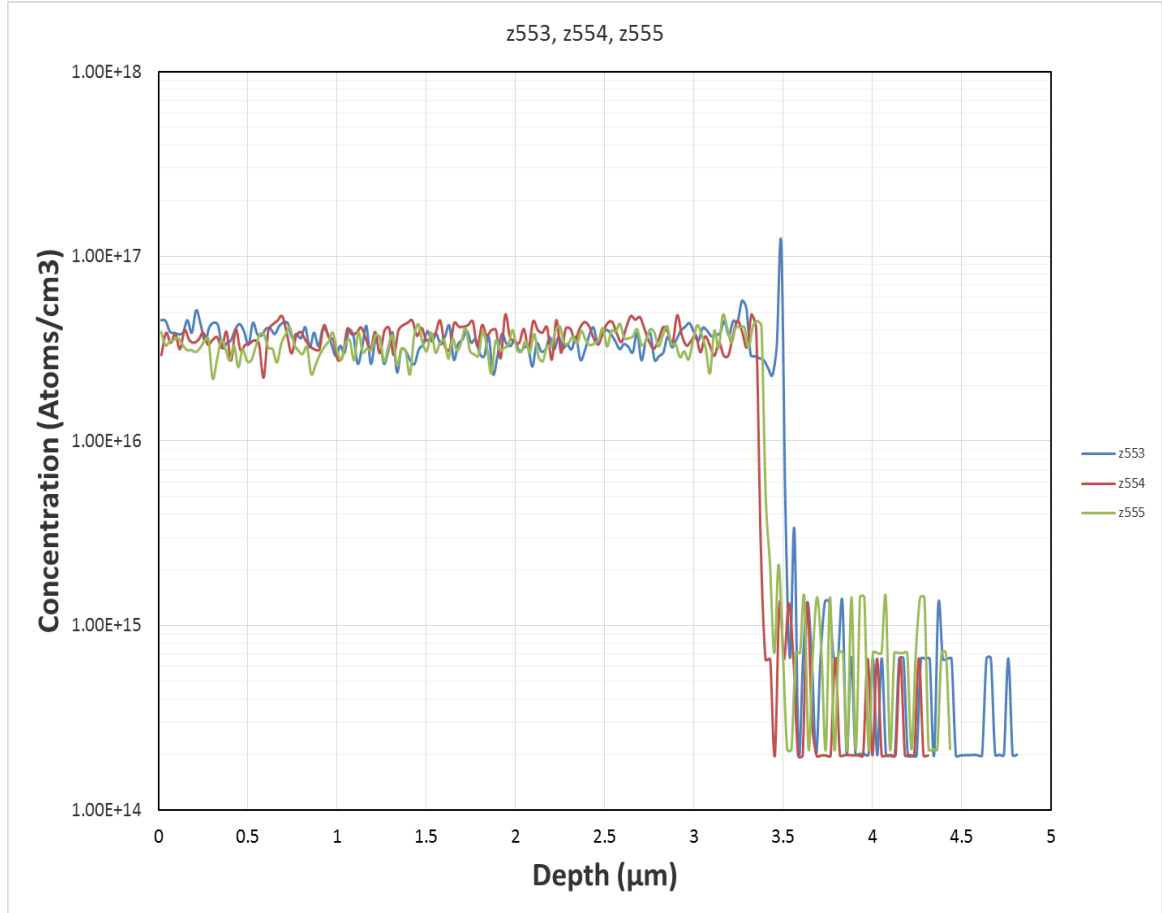


Figure 77. CdTe samples, z-553, z-554, and z-555, were grown at 250 °C, 240 °C, and 230 °C respectively with a Cd₃As₂/CdTe BEP ratio of 1.0 using CdTe (100) substrate.

Also, the effect of Zn incorporation on As incorporation was studied in samples grown using the Cd₃As₂ cracker. As-doped Cd_{0.96}Zn_{0.04}Te samples (z-559, z-560, and z-561) were grown on Cd_{0.96}Zn_{0.04}Te (100) substrates at 250 °C, 240 °C, and 230 °C, respectively, while other growth parameters, such as a Cd₃As₂/CdTe BEP ratio of ~ 1.0 , a Cd/CdTe BEP ratio ~ 0.3 , and a Zn/CdTe ~ 0.04 , were kept constant. The SIMS results of these samples were presented in Figure 78, which shows As incorporation of $\sim 7 \times 10^{16}$ atoms/cm³ with no evidence of structural degradation. Just like the case of doping

ordinary CdTe, temperature changes within the 230 °C to 250 °C range did not affect doping incorporation, suggesting that As incorporation is not sensitive to temperature change in the 230 °C to 250 °C range. The most significant results from the use of the cracker cell is that As incorporation higher than the incorporation level attained with the use of the effusion cell can be achieved with good structural quality at higher growth temperatures.

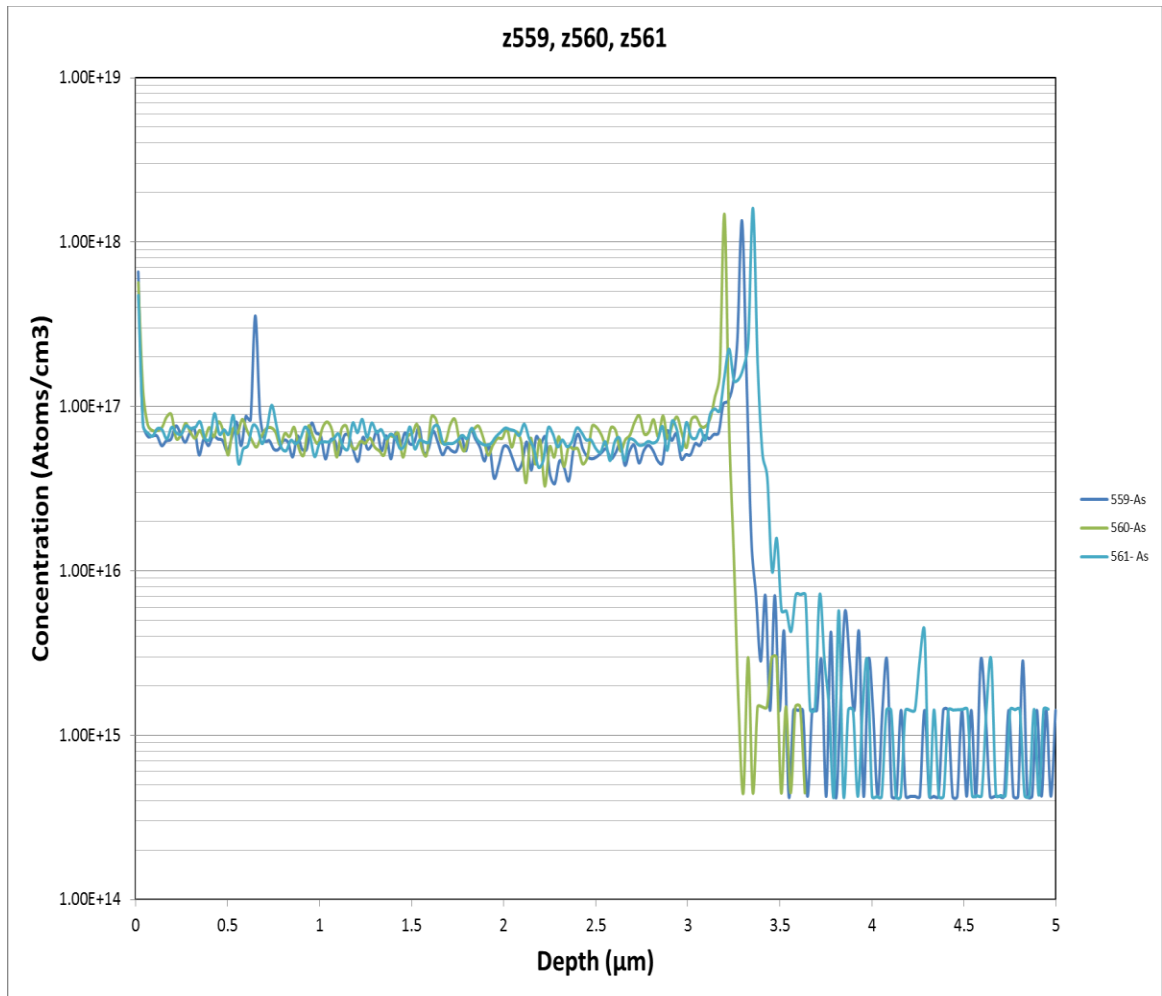


Figure 78. Cd_{0.96}Zn_{0.04}Te samples, z-553, z-554, and z-555, were grown at 250 °C, 240 °C, and 230 °C, respectively, with Cd₃As₂/CdTe BEP ratio of 1 using Cd_{0.96}Zn_{0.04}Te (100) substrate.

The issue of sample degradation and rapid increase in As incorporation observed in some samples at the initial phase was not observed in the final phase of this project as doping at higher temperatures leads to controllable As incorporation at technologically important levels.

4.3.2.3 *As activation*

Achieving p-type conduction in doping of HgCdTe with arsenic using MBE has been reported to be challenging due to its ability to reside on metallic and non-metallic sub-lattice sites.¹¹⁴ The desired result of arsenic doping of HgCdTe is for As atom to substitute on the Te site, but the As atoms have been reported to occupy cation or interstitial sites, thereby making them act as donors or neutral complexes.^{53, 115, 116} Hence, a high temperature annealing after MBE growth is required to move As atoms to Te sites.¹¹⁷ Similar ex-situ thermal annealing has been used to activate As dopants in CdTe.^{13, 44}

Following the successful control of As incorporation, activation annealing studies were conducted. Hall measurements and CV measurements were used to study activation in As-doped CdTe. Hall measurements provided somewhat unreliable hole-density measurements, thus CV was mostly used in As-activation studies because depth doping profile is easily obtained along with carrier concentration measurement in CV.

CdTe:As and CdZnTe:As structures were annealed under different conditions using ampoule annealing and rapid thermal process (RTP). All ampoule anneals were performed under Cd overpressure while RTP was done without Cd overpressure. Annealing temperatures ranged from 450 °C to 600 °C, and annealing time ranged from

thirty seconds to thirty minutes. Hall measurements were used for structures that only had absorber layers deposited on the substrate and were yet to be used for device integration. Hole concentration of low 10^{15} cm^{-3} to low 10^{16} cm^{-3} was consistently achieved for structures that were annealed prior to being used for device fabrication, and the carrier lifetime measured for most of these samples was $\sim 2 \text{ ns}$.

As activation by RTP was compared to ampoule anneals with a Cd overpressure at varying temperatures as shown in select samples in Table 13. Most of the samples were grown with estimated an carrier concentration $\sim 1 \times 10^{17} \text{ cm}^{-3}$.

Table 13. Carrier concentration of As-doped structures measured by Hall effect technique after activation annealing.

Film	Activation process	N (/cm ³) by Hall measurement
CdTe:As	Ampoule annealing at 500 °C, 10 min	$\sim 8.47 \times 10^{16}$
CdTe:As	Ampoule annealing at 500 °C, 10 min	$\sim 2.84 \times 10^{16}$
CdTe:As	Ampoule annealing at 500 °C, 10 min	$\sim 1.02 \times 10^{16}$
CdZnTe:As	Ampoule annealing at 500 °C, 10 min	$\sim 6.0 \times 10^{15}$
CdZnTe:As	Ampoule annealing at 500 °C, 10 min	$\sim 2.3 \times 10^{15}$
CdTe:As	Ampoule annealing at 550 °C, 10 min	$\sim 5 \times 10^{15}$
CdTe:As	Ampoule annealing at 550 °C, 10 min	$\sim 6 \times 10^{15}$
CdTe:As	RTP at 450 °C, 1 min	$\sim 8 \times 10^{15}$
CdTe:As	RTP at 450 °C, 10 min	$\sim 2 \times 10^{15}$
CdTe:As	RTP at 450 °C, 20 min	$\sim 1.5 \times 10^{15}$
CdTe:As	RTP at 550 °C, 30 sec	$\sim 1 \times 10^{15}$
CdTe:As	RTP at 550 °C, 1 min	$\sim 6 \times 10^{15}$
CdZnTe:As	RTP at 550 °C, 1 min	$\sim 5 \times 10^{15}$
CdZnTe:As	RTP at 600 °C, 30 sec	$\sim 8 \times 10^{15}$

Ampoule annealing seems to show higher carrier concentration than RTP, as expected. The slightly lower carrier concentration in RTP may be attributable to Cd desorption at the temperatures required for activation (500 °C-600 °C) since RTP is done without Cd overpressure. This Cd desorption in RTP can create Cd vacancies, which may

compensate some of the carriers, but RTP is significantly faster, enabling higher throughput and faster screening.

Although samples annealed with ampoule annealing seem to have a slightly higher carrier concentration, samples annealed with RTP show better results for device parameters when the structures are used to make devices as discussed in section 5.

4.4 Diffusion studies in CdTe

Dopants can move from the site of incorporation during or after growth especially under high temperature conditions. This is an undesirable effect that can destroy structures. The redistribution process can either be anisotropic, which takes place due to energy gradients, or isotropic in nature. Common mechanisms of impurities in redistribution are diffusion, which is isotropic in nature, and segregation, which is anisotropic in nature.⁶⁷

Diffusion of impurities in semiconductors occurs when impurity atoms, which are thermally energized, hop randomly. Vibration of the impurity atom is an attempt for the atom to hop from the lattice site, which gives the attempt rate as a function of time. The diffusion hop is directly proportional to the attempt rate and the probability of a successful hop. The diffusion of the impurity in a host system is measured by a constant called the diffusion coefficient, D , which depends on the rate of successful diffusion hops and the average hop length of the impurity atoms. The diffusion coefficient, D , of dopants can be expressed mathematically as ⁶⁷

$$D = D_o e^{-\Delta E/kT} \quad (4.5)$$

where ΔE is the energy barrier that the atom must overcome for diffusion to occur, k is the Boltzman constant, and T is the temperature of the dopants. D_0 is the diffusion constant if all hop attempts were successful $\Delta E = 0$.

In order to study the diffusion profile of impurities used in this project, selected MBE-grown layers of interest were annealed at specific temperatures. The annealing experiments for this study were done mostly in a sealed ampoule with a Cd overpressure. SIMS measurements of annealed samples were taken and compared to SIMS measurements of as-grown samples, which were taken from a separate piece of the same epilayer. Diffusion models based on analytical solution methods were used to reconstruct the SIMS data profiles in order to estimate the diffusion coefficients of the dopant materials in the annealed samples. In this project, there were two types of profiles for the initial concentration distribution of the dopant materials that were studied for diffusion. These profiles are of a step-function form. The distribution profile for each of the dopant materials studied was either a one-dimensional step-function distribution form (shown in Figure 79) or in the form of superposition of two displaced step-function distributions (shown in Figure 80) in their initial condition.

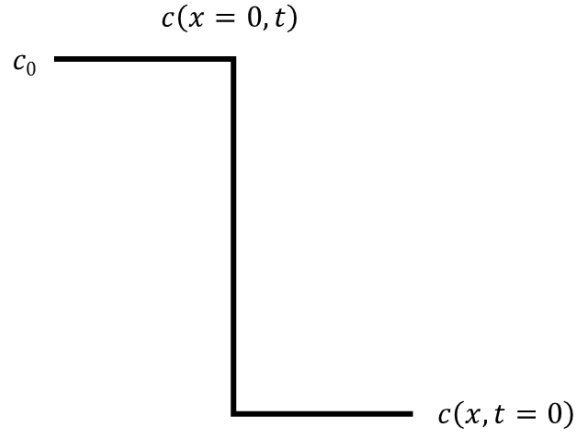


Figure 79. One-dimensional step-function initial conditions for one-dimensional diffusion along x .¹¹⁸

This step function in Figure 79 leads to the solution that describes the diffusion in a semi-infinite body where the surface concentration is constant. The initial and boundary conditions for this step-function are given as

$$c(x = 0, t) = c_0 \quad (4.6)$$

$$\frac{\partial c}{\partial x}(x = \infty, t) = 0 \quad (4.7)$$

$$c(x, t = 0) = 0 \quad \text{for } 0 \leq x < \infty \quad (4.8)$$

and the error function solution to this one-dimensional step function initial condition is given as

$$c(x, t) = c_0 \left[1 - \operatorname{erf} \left(\frac{x}{\sqrt{4Dt}} \right) \right] \quad (4.9)$$

where c_0 is the initial concentration, D is the diffusion coefficient (also referred to as diffusivity), t is the annealing time, and x is distance.

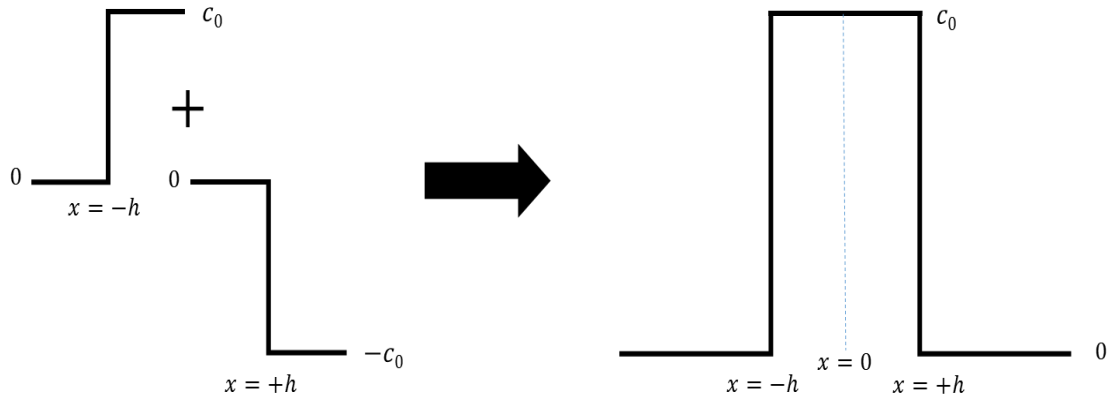


Figure 80. Superposition method for constructing confined source for one-dimensional diffusion along x .¹¹⁸

The superposition of two step-function distributions as shown in Figure 80 leads to the solution that describes the diffusion in a semi-infinite body from a substance that was initially confined in the region of $-h \leq x \leq +h$, where Δx is the thickness of the source. The initial and boundary conditions for this step-function is given as

$$c(x, t = 0) = \begin{cases} c_0 & -h < x < +h \\ 0 & +h \leq x < \infty \end{cases} \quad (4.10)$$

and the error function solution

$$c(x, t) = \frac{c_0}{2} \left[\operatorname{erf} \left(\frac{x+h}{\sqrt{4Dt}} \right) - \operatorname{erf} \left(\frac{x-h}{\sqrt{4Dt}} \right) \right] \quad (4.11)$$

Diffusivities were determined from these models by recreating the after-annealing concentration depth profile using these error function solutions. It was assumed that the total number of atoms was constant before and after diffusion.

Impurity redistribution can affect the doping profile of a material system. For example, if the diffusion coefficient increases at high impurity concentrations, the maximum dopant concentration attainable can be limited.⁶⁷ Generally, effects of

excessive dopant diffusion ¹¹⁹ and segregation ⁶⁷ can distort the well-defined impurity distribution, degrading electrical properties of the host material.

4.4.1 Magnesium in CdTe

4.4.1.1 Modeling prediction of Mg diffusion in CdTe

Mg has been reported to be a fairly fast diffusant. Mg has shown a lot of promise as a material for forming CdMgTe barriers in CdTe structures. Excessive diffusion of Mg in CdTe/CdMgTe DH can lead to increased defect density, thereby degrading the overall properties of the device and affecting its operation due to the impact of defects on carrier recombination at a high defect density.¹²⁰ Mg diffusion in CdTe was modeled based the on the activation energy and diffusivities reported by Seweryn et al.¹²¹ The parameters for the modeling are presented in Table 14, and the results of the modeling show the redistribution of Mg atoms into their surroundings as depicted in Figures 81 and 82.

Table 14. Modeling parameters for Mg diffusion simulation.

Modeling parameters	
Diffusivity at 300 0C (cm ² /s)	7.79283E-19
Diffusivity at 400 0C (cm ² /s)	1.01649E-16
Diffusivity at 500 0C (cm ² /s)	3.76093E-15
Time (s)	600
Case 1 CdMgTe thickness (nm)	30
Case 2 CdMgTe thickness (nm)	100

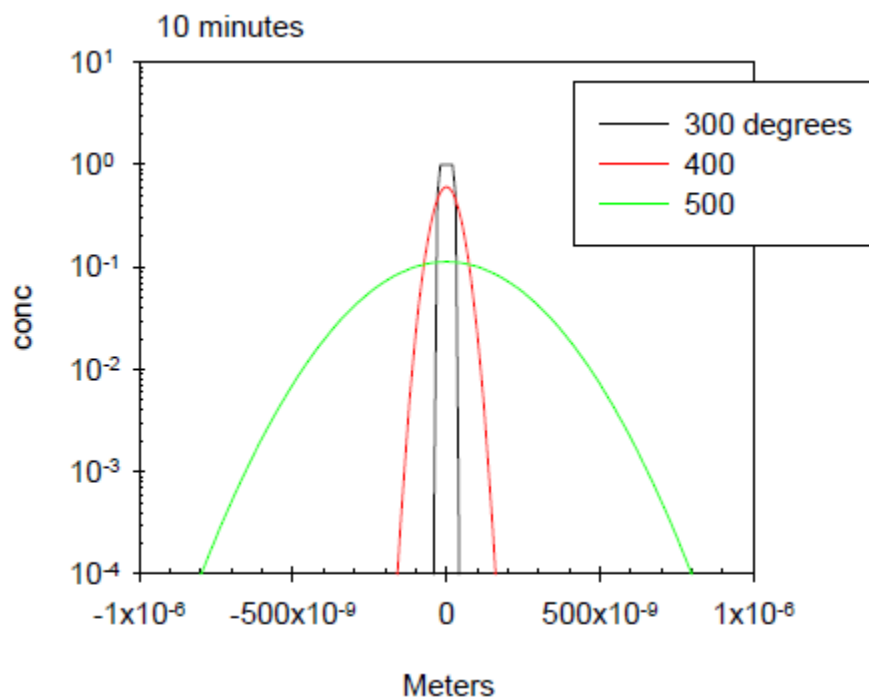


Figure 81. Modeling of Mg diffusion in 30 nm-thick CdMgTe when annealed at 300 °C, 400 °C, and 500 °C for 10 minutes.

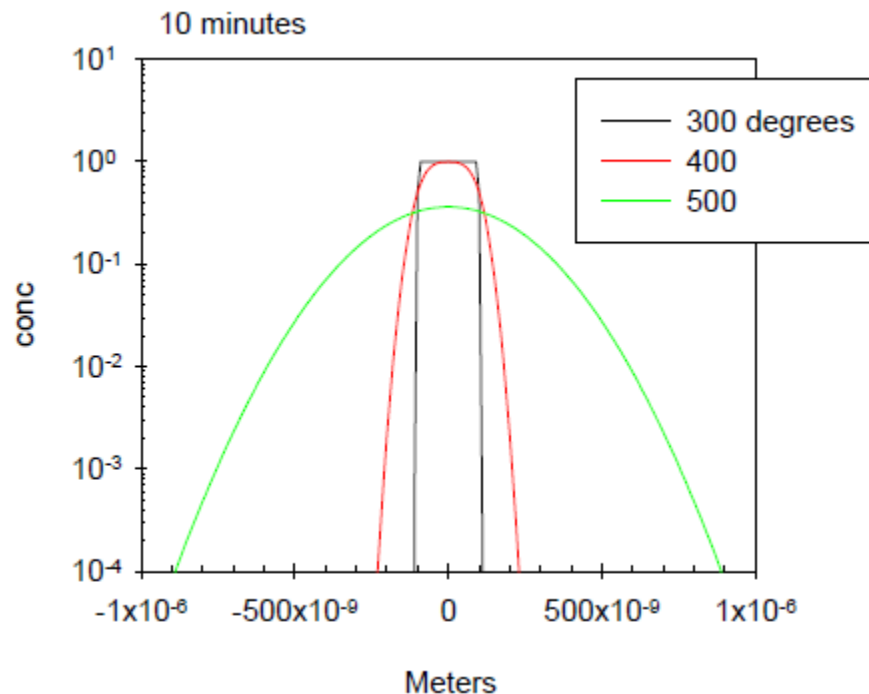


Figure 82. Modeling of Mg diffusion in 100 nm-thick CdMgTe when annealed at 300 °C, 400 °C, and 500 °C for 10 minutes.

4.4.1.2 *Experimental measurement of Mg diffusion in CdTe*

The CdMgTe/CdTe SH structure was annealed at 350 °C for thirty-six hours, 400 °C for three and a half hours, and 500 °C for ten minutes under Cd overpressure. As shown in Figure 83, the concentration-depth profile measured by SIMS at these annealing temperatures was compared to as-grown samples that were pieces from the sample epilayer as the annealed samples. The concentration-depth profile of the 350 °C annealing is nearly identical to the as-grown concentration depth profile, suggesting that there was not significant atom redistribution in the 350 °C annealing; noticeable atom redistribution can be seen in the 400 °C-annealing and more pronounced atom redistribution seen in the 500 °C annealing. An asymmetric fast diffusion was observed on the substrate side of the SH annealed at 500 °C, which is significantly more pronounced than SIMS artifacts due to memory effects observed in the other three profiles. The cause of this asymmetric fast diffusion is not clear at this point.

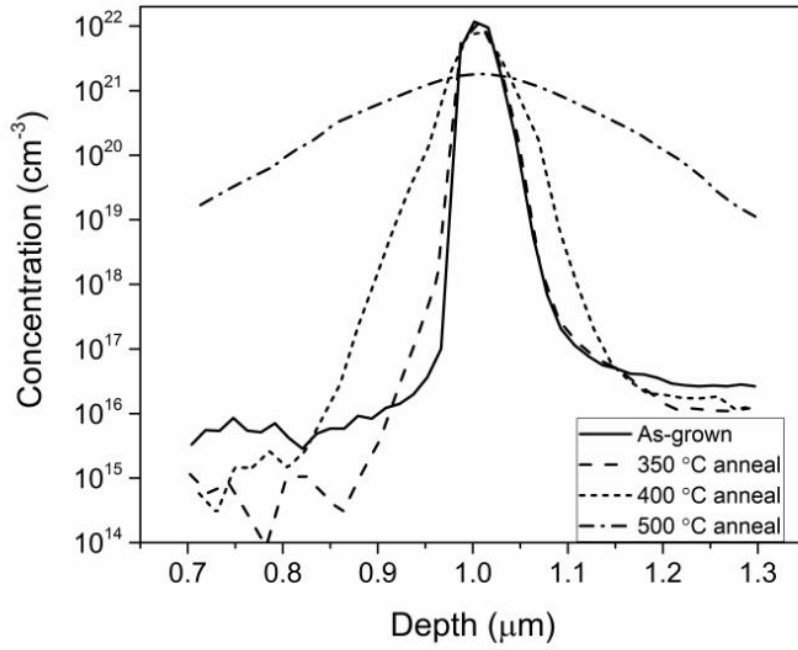


Figure 83. Comparison of Mg concentration depth profile in CdMgTe/CdTe single heterostructures for an as-grown sample, and samples annealed at 350°C for 36 h, 400°C for 3.5 h, and 500°C for 10 min.

The SIMS profiles measured following diffusion anneals were fit with a model to determine the diffusion coefficients (D). Mg diffusion in a typical CdMgTe/CdTe heterostructure was modeled as shown in Figure 84.

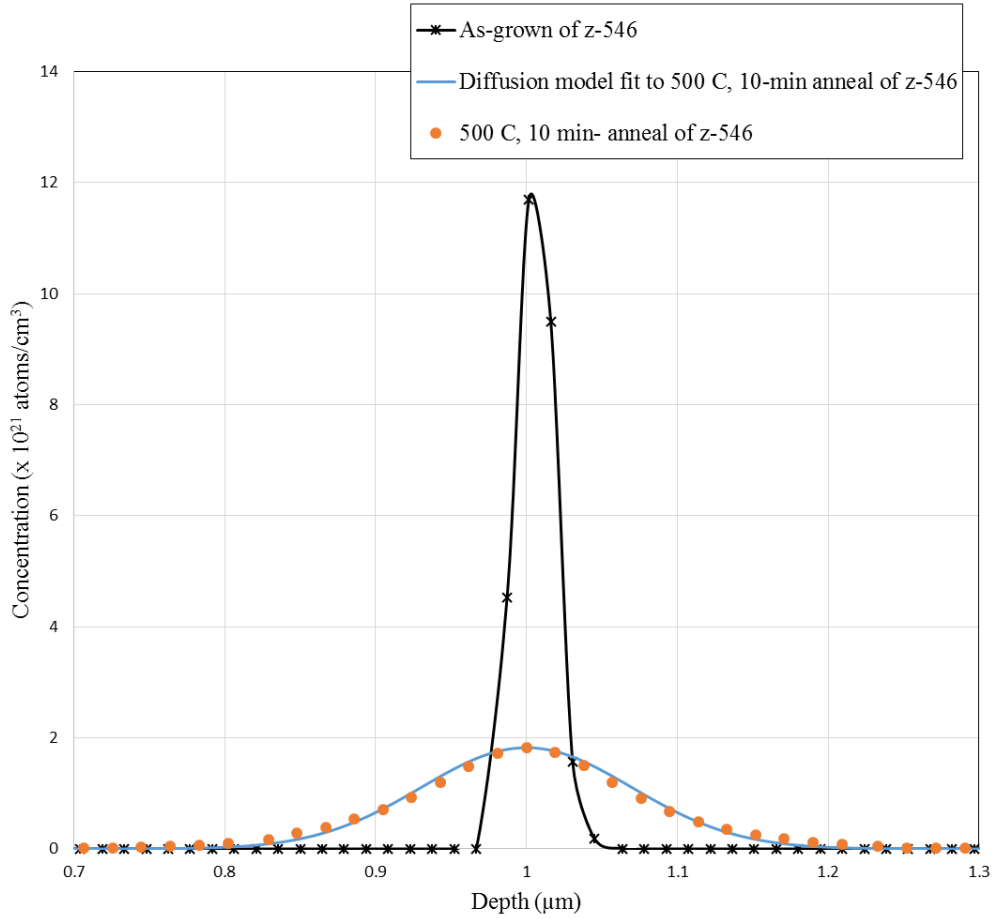


Figure 84. Diffusion model fit for determination of diffusion coefficient for a CdMgTe/CdTe single heterostructure annealed at 500 °C for 10 min.

The CdMgTe/CdTe heterostructure consist of a CdMgTe thin-film layer, which was initially bounded by two CdTe layers. This model, given as equation 4.14, is based on the analytical solution of the diffusion equation for a material that was initially confined within two semi-infinite boundaries.¹²²

A modeled diffusion coefficient for the 500 °C annealing is $\sim 4.0 \times 10^{-14} \text{ cm}^2\text{s}^{-1}$, and the 400 °C-annealing is estimated to be around $\sim 7.0 \times 10^{-17} \text{ cm}^2\text{s}^{-1}$ while the assumed upper bound diffusion coefficient for the 350 °C annealing is $\sim 3.5 \times 10^{-18} \text{ cm}^2\text{s}^{-1}$. As shown in Figure 85, diffusion coefficient values for 350 °C and 400 °C are slightly lower than the values reported by Seweryn et al. [42] where CdMgTe structures were grown

under Cd-rich and Te-rich conditions. This group annealed MBE-grown samples under dry nitrogen flux. For this study, the measured D at 500 °C was considerably higher.

The effect of lattice strain on interdiffusion was investigated by using a (100)-oriented $\text{Cd}_{0.96}\text{Zn}_{0.04}\text{Te}$ substrate to grow a supposedly 100-nm thick $\text{Cd}_{0.65}\text{Mg}_{0.35}\text{Te}$ that was capped with 100-nm thick CdTe. The lattice parameters of the $\text{Cd}_{0.65}\text{Mg}_{0.35}\text{Te}$ film and the $\text{Cd}_{0.96}\text{Zn}_{0.04}\text{Te}$ are close enough to give near-lattice-match condition. The $\text{Cd}_{0.96}\text{Zn}_{0.04}\text{Te}/\text{Cd}_{0.65}\text{Mg}_{0.35}\text{Te}$ structure was annealed at 500 °C for ten minutes under Cd-rich conditions in the same ampoule as the above $\text{CdTe}/\text{Cd}_{1-x}\text{Mg}_x\text{Te}$ SH. The $\text{Cd}_{0.65}\text{Mg}_{0.35}\text{Te}$ structure-grown $\text{Cd}_{0.96}\text{Zn}_{0.04}\text{Te}$ substrate has a lower diffusion coefficient at 500 °C when compared to both Seweryn et al., and the results obtained on the $\text{Cd}_{0.65}\text{Mg}_{0.35}\text{Te}/\text{CdTe}$ S.H grown on (100)-oriented CdTe at the same temperature suggest that either the absence of lattice strain or the presence of a small amount of Zn can slow down the rate of interdiffusion. It was noted that this $\text{Cd}_{0.65}\text{Mg}_{0.35}\text{Te}$ structure grown on $\text{Cd}_{0.96}\text{Zn}_{0.04}\text{Te}$ substrate has two diffusion components on the substrate side—a fast diffusion component and a slower diffusion component—as shown in Figure 86. The slower diffusion component has $D \sim 1.8 \times 10^{-15} \text{ cm}^2\text{s}^{-1}$ and the fast diffusion component has $D \sim 2.1 \times 10^{-11} \text{ cm}^2\text{s}^{-1}$. The origin of the fast diffusion coefficient is not clear, but it was well fitted by assuming the diffusion from a constant plane source of Mg with a surface concentration of $1.3 \times 10^{20} \text{ cm}^{-2}$. A similar diffusion of Zn into the $\text{Cd}_{1-x}\text{Mg}_x\text{Te}$ layer was not observed. In addition, Mg was observed to diffuse into the CdTe overlayer at a slower rate than it did in the $\text{CdTe}/\text{Cd}_{0.65}\text{Mg}_{0.35}\text{Te}$ SH with $D \sim 4.0 \times 10^{-15} \text{ cm}^2\text{s}^{-1}$, which is comparable to the results of Seweryn et al. at 500 °C. These results suggest that the combination of Zn alloying and lattice matching can inhibit Mg diffusion CdTe.

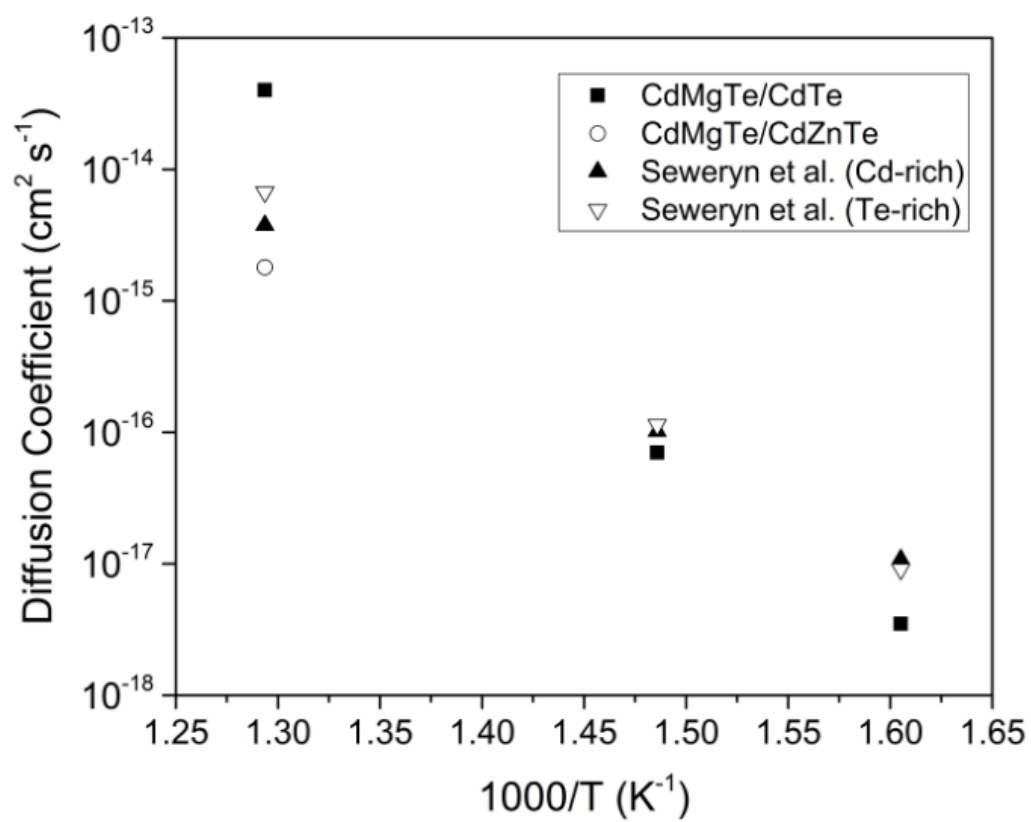


Figure 85. Comparison of Mg diffusivity in CdTe for various conditions.

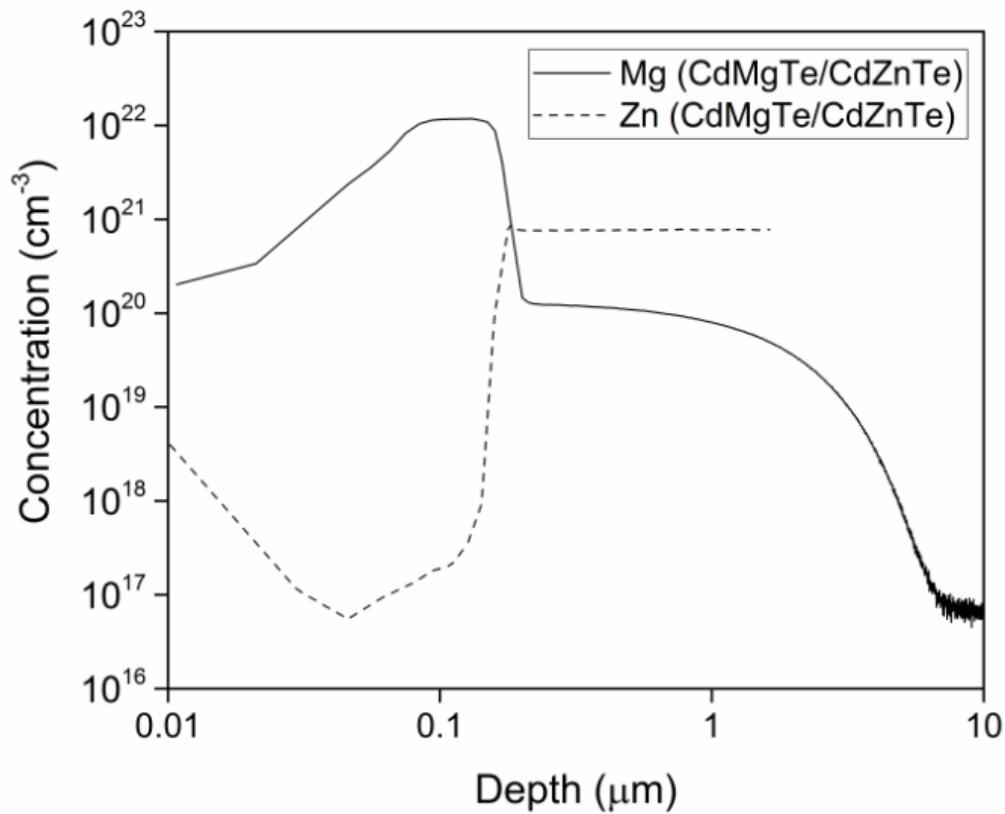


Figure 86. SIMS profile of CdTe/Cd_{0.65}Mg_{0.35}Te/Cd_{0.96}Zn_{0.4}Te structure after a 500°C annealing for 10 min showing two diffusion components into the CdZnTe.

4.4.2 Iodine-Doped CdTe

4.4.2.1 Iodine in CdTe

High temperature processing is often needed for the p-type side of solar cells, therefore the n-type side has to be able to withstand the temperature demand. Activation annealing was done for arsenic, and its impact on carrier lifetime was studied while thermal anneals were done on iodine to examine them for thermal stability at temperatures higher than the annealing temperature of As.

Thermal anneals were carried out in quartz ampoules containing the samples and a small piece of Cd that were sealed under vacuum. This allowed annealing experiments

to be done under isothermal Cd overpressure conditions at temperatures up to 600 °C to determine iodine stability in MBE-grown CdTe crystal.

I-doped CdTe was annealed at 500 °C for twelve hours and at 600 °C for twenty-four hours in sealed ampoules under Cd over pressure to evaluate the process compatibility of iodine as a dopant in MBE-grown CdTe. The results of these thermal anneals, as shown in Figure 87, indicate that there is little change in the concentration-depth profile of the annealed samples from that of the un-annealed samples, which are pieces from the same epilayer, as characterized by SIMS. Modeling this minimal change in the concentration-depth profile of the 600 °C, twenty-four-hour annealed sample indicates an I diffusion of $\sim 1.4 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1}$. This result suggests that iodine is not a fast-diffusing dopant in epitaxial CdTe. The thermal stability result reported here is consistent with the results obtained in I-doped HgCdTe grown by MOCVD,¹²³ and by MOVPE.¹²⁴

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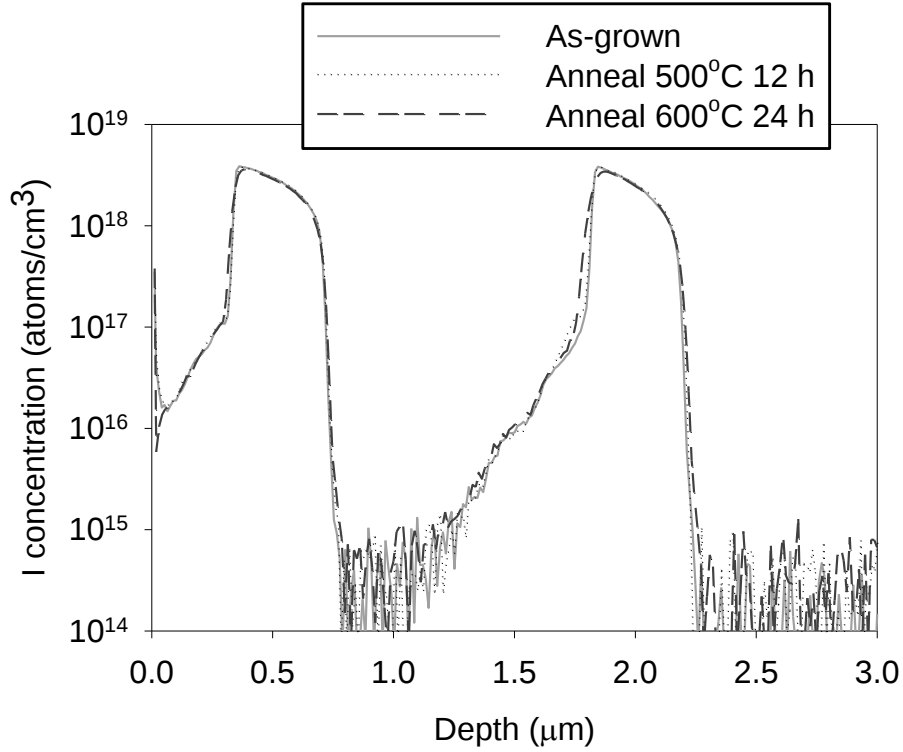


Figure 87. SIMS profile of an as-grown and an annealed iodine step-doped CdTe sample.

4.4.2.2 Iodine in As-doped CdTe

Further investigations were carried out to test the thermal stability behavior of iodine in a p-n epitaxial structure by annealing a sample that consist of iodine-doped CdTe steps in a uniformly As-doped CdTe layer at 600 °C for twenty-four hours under Cd overpressure. SIMS profiles from un-annealed and annealed samples, which are pieces from the same epilayer, are shown in Figure 88.

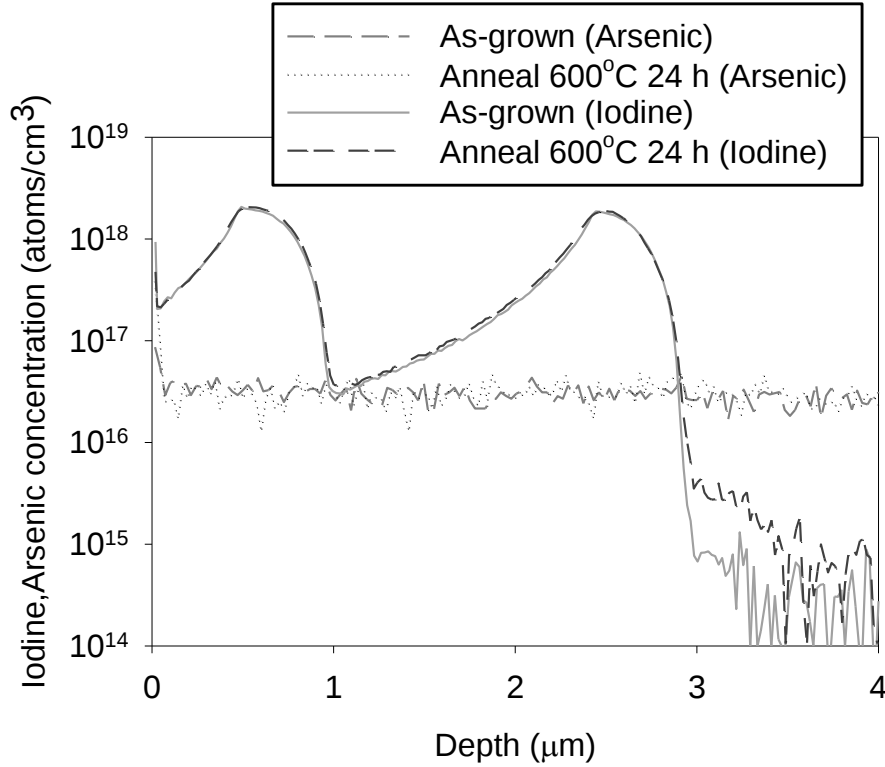


Figure 88. SIMS profile of an as-grown and an annealed iodine step-doped CdTe:As sample.

This sample also suggests that the redistribution of iodine atoms after this annealing is small. The SIMS profile shows that As does not segregate due to the presence of I. Also, it shows that iodine diffusion is minimal for the 600 °C, twenty-four-hour annealing, suggesting doping levels of As do not affect the I diffusion, but surface accumulation during the growth of I-doped CdTe was noticed just as it was noticed in some sample profiles. This surface accumulation was accentuated during As co-doping, as shown by the non step-like I profiles, yet iodine remains stable to diffusion at annealing temperatures up to 600 °C. Modeling the slight differences between as-grown samples and the 600 °C, twenty-four-hour annealed sample indicates an I-diffusion coefficient of $\sim 5.2 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1}$ at 600 °C. This result suggests that iodine will likely not diffuse across p-n junctions in devices, unlike indium, which was reported by Watson et

al.¹²⁶ to have a diffusion coefficient of $\sim 3.3 \times 10^{-15} \text{ cm}^2\text{s}^{-1}$ at 400 °C and $\sim 2.0 \times 10^{-11} \text{ cm}^2\text{s}^{-1}$ at 600 °C under Cd saturation conditions. Also, this reinforces the suggestion that iodine may be the preferred dopant for highly doped n-type CdTe.

4.5 Summary

4.5.1 Iodine doping

Heavy doping of CdTe can be achieved with iodine without degrading important properties that are useful for photovoltaic application. The n-type doping of CdTe can be accomplished with iodine up to nearly 10^{19} cm^{-3} . It might be possible to achieve a slightly higher maximum doping concentration, but the effect of the doping concentration limiting mechanisms becomes apparent at concentrations above $2 \times 10^{19} \text{ cm}^{-3}$. Doped DHs have a lifetime well in excess of the radiative lifetime due to the photon-recycling effect. This is consistent with what was observed for doped GaAs/AlGaAs DHs, emphasizing that, once surface recombination is controlled, the electronic properties of CdTe are comparable to those of GaAs with the potential benefits of a slightly lower radiative recombination parameter and a higher tolerance to dislocations.

These iodine-doped samples show long lifetimes with evidence of photon-recycling effects and no evidence of PL degradation, which is in contrast to indium doped material as it exhibits significant non-radiative recombination at carrier concentration above $5 \times 10^{16} \text{ cm}^{-3}$.¹²⁷ Thermal annealing studies of some of these samples suggest that iodine is stable against redistribution at temperatures up to 600 °C under Cd over pressure conditions. Iodine will likely not diffuse across a p-n junction in devices, unlike indium, which has been reported to do so more quickly.¹ This result, coupled with the longer

lifetimes observed for I-doping compared to equivalent In-doping concentrations, suggests that iodine may be the preferred dopant when compared with indium.

CdMgTe alloy has been doped with similar success, exhibiting a donor activation energy (E_a) ranging from 17 meV for $x \sim 0.25$ to approximately 58 meV for $x \sim 0.35$. Iodine has been shown to have significant advantages as a dopant of choice over In for highly n -type doped CdTe.

4.5.2 Arsenic doping

Intentional dopants in semiconductors usually range 10^{16} to 10^{19} cm⁻³ in atomic density in a host semiconductor, making the host semiconductor to be greater than the dopant by a factor of 10^4 to 10^7 . As-doped CdTe with a dopant concentration above mid- 10^{17} cm⁻³ shows precipitation of either As or As₂Te₃, indicating its solubility limit to be around this value. APT measurements indicate that As is spatially segregated throughout the film and tends to cluster in areas of high concentrations, which degrades the sample structure. Stable and reproducible As incorporation of $\sim 1 \times 10^{17}$ atoms/cm³ was achieved in CdTe without structural degradation with the use of a custom low-flux Cd₃As₂ cracker. High temperature thermal activation annealing was used to consistently produce acceptors $\sim 2 \times 10^{16}$ atoms/cm³ in grown CdTe:As and CdZnTe:As structures. As incorporation and activation levels achieved in this studies should be sufficient for device fabrication.

5. DEVICE FABRICATION

5.1 Device structures

Film structures grown at Texas State University were sent to the National Renewable Energy Laboratory for the purposes of making device structures. These devices were intended to demonstrate that high V_{oc} can be achieved through high net acceptor density and lifetime. The device structure used in these studies is as shown in Figure 89.

ZnO:Al	~120 nm
i-ZnO	100 nm
CdSeTe, CdSeTe:I, CdMgTe:I, CdS:In, Zn-Mg-O, CdTe:In	~40 nm
p-type CdTe:As <i>or</i> CdZnTe:As	3 μm
CdTe <i>or</i> CdZnTe	substrate
Cu	1-2 nm
Mo	350-500 nm

Figure 89. Device structure used in these studies.

The film structures used for these devices are either 3 μm -thick CdTe:As or CdZnTe:As absorbers. These films were annealed to activate the As acceptors prior to device fabrication using either ampoule annealing or RTP. The films were then etched

with 0.1% Br:MeOH solution to remove $\sim 0.2 \mu\text{m}$ from the surface. The etch process is needed since the annealing process can lead to surface pitting, which can lead to structural degradation in the emitter growth. Etched films are loaded into the MBE for emitter growth. Cu/Mo was used for the back contact to the substrate, and an emitter, O/ZnO/ZnO:Al front contact stack was used for devices.

The sample set comprising z-498, z-499, z-500, z-501, z-502, z-503, and z-504 was annealed with an ampoule annealing process prior to their use in device fabrication. Samples z-498, z-499, z-500, and z-501 have a CdZnTe:As film while samples z-502, z-503, and z-504 have a CdTe:As film. The J-V characteristics of the devices made from this sample set are presented in Figure 90.

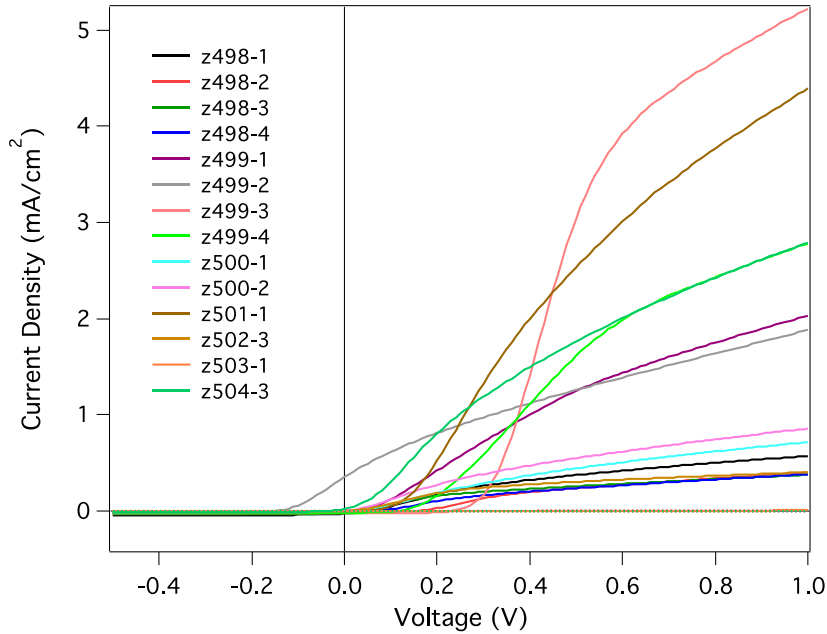


Figure 90. J-V characteristics for devices made with samples z-498, z-499, z-500, z-501, z-502, z-503, and z-504 with different emitters, which were annealed with ampoule annealing process prior to device fabrication.

Another sample set comprising z-611, z-612, z-613, z-614, and z-615 with CdZnTe:As films was used to fabricate device structures with varying emitters. The J-V

curve for z-611 with a CdSeTe emitter, z-612 with a CdSeTe:I emitter, and z-615 with a CdMgTe:I emitter is shown in Figure 91.

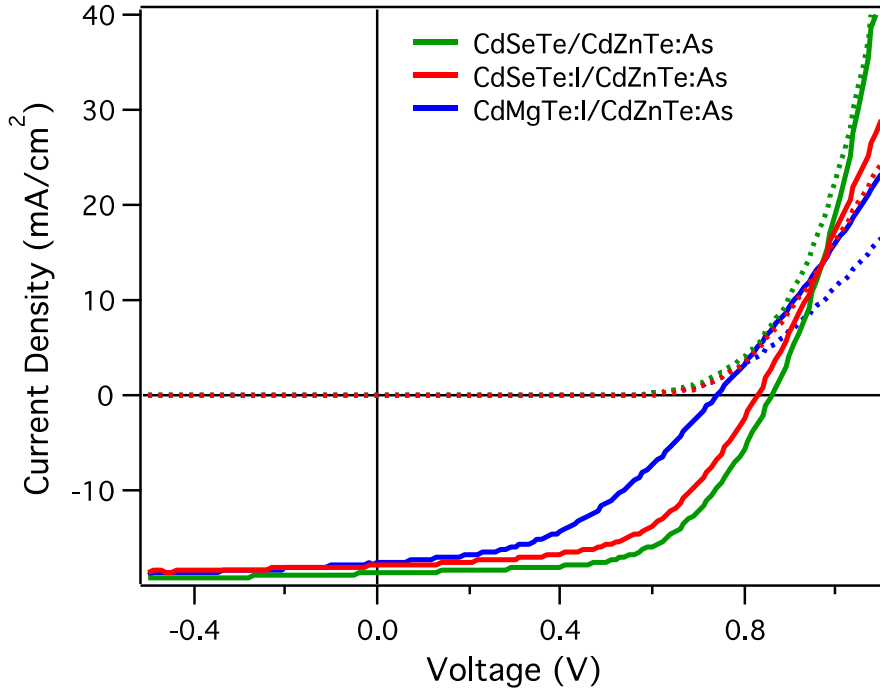


Figure 91. J-V characteristics for devices made with samples z-611(green line), z-612 (red line), and z-615 (blue line) with different emitters, which were annealed with RTP prior to device fabrication.

The curves of diode-like J-V characteristics from Figure 91 show higher V_{oc} compared to the curves shown in Figure 90, which indicates a higher V_{oc} for samples annealed with a RTP process than samples annealed with an ampoule annealing process prior to making devices. These results suggest that an RTP process is better for structures that will be used for making devices.

CV measurements for devices made from CdTe:As and CdZnTe:As films have consistently show a hole density $\geq 10^{15}$ - 10^{16} cm^{-3} and $\geq 10\%$ activation as shown in Figure 92. The highest hole density at As concentration of 2×10^{16} cm^{-3} with $\sim 100\%$

activation suggests that the doping limit for the growth conditions used in this project might be around $2 \times 10^{16} \text{ cm}^{-3}$.

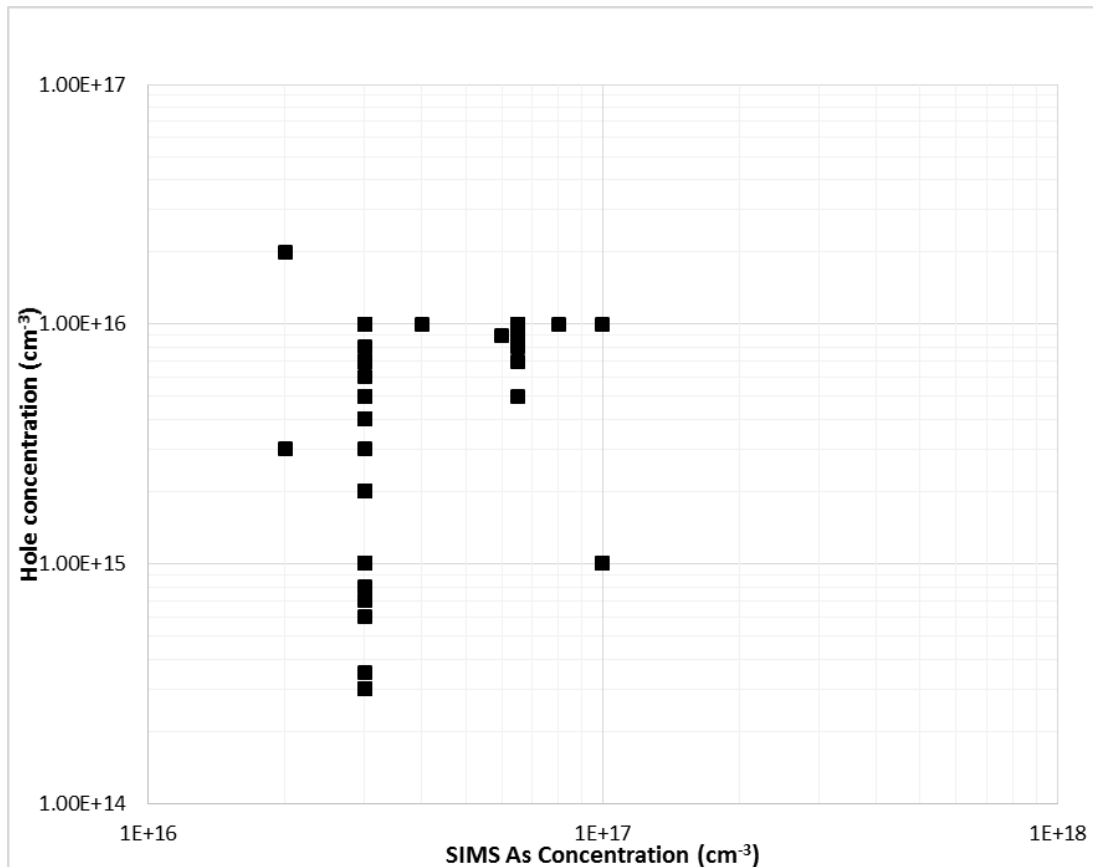


Figure 92. C-V-measured activated hole concentration vs. calibrated SIMS iodine concentration for arsenic-doped CdTe.

The CV profiles of the device structures made with the sample set comprising z-611, z-612, z-613, z-614, and z-615 are shown in Figure 93. These profiles show a narrow depletion width to indicate a high hole concentration has a flat profile, which suggests less As outdiffusion. Basic solar cell parameters for select device structures were selected from this set to show the best results obtained with different emitters, which is presented in Table 15.

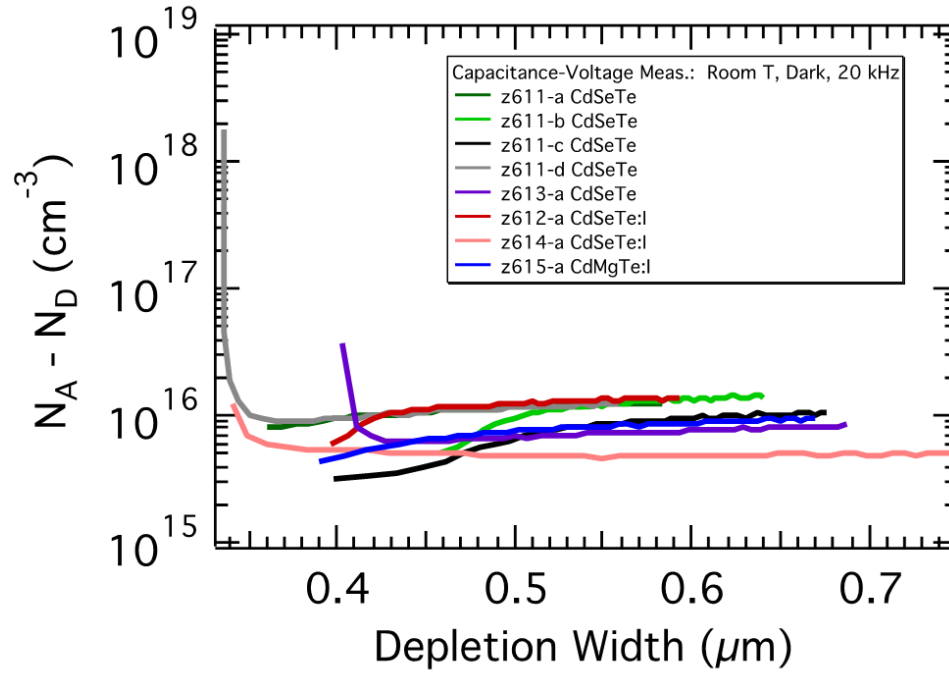


Figure 93. C-V profile of device structures for sample set comprising z-611, z-612, z-613, z-614, and z-615 using different emitters.

Table 15. Basic solar cell parameters for device structures made with samples z-611(CdSeTe emitter), z-612 (CdSeTe:I), and z-615 (CdMgTe:I) with different emitters, which were annealed with RTP prior to device fabrication.

emitter	J _{sc} (mA/cm ²)	V _{oc} (mV)	FF (%)	η (%)	N _A – N _D (cm ⁻³)
CdSeTe	18.5	880	59	9.4	10 ¹⁶
CdSeTe:I	17.7	829	56.8	8.2	8x10 ¹⁵
CdMgTe:I	17.5	741	47	5.8	high 10 ¹⁵

The minority carrier lifetimes of ~2 ns measured in most of these device structures is similar to the minority carriers measured in their film structures before they were used to make device structures. The most significant result achieved in the device structure is a V_{oc} of 880 mV.

5.2 Summary

Among ~450 samples that were grown over the course of this project, few samples were designed for device fabrication. These samples were sent to NREL where they were used for fabricating devices. Some of the important properties of these devices were measured in order to demonstrate that surface passivation and increase in doping can increase V_{oc} in CdTe solar cells. A hole-carrier concentration of 10^{16} atoms/cm³ was consistently achieved in CdTe:As and CdZnTe:As films and in device structures made with these films. Carrier lifetimes of ~2 ns were achieved in both films and devices. V_{oc} as high as 880 mV and a fill factor as high as ~60% was achieved in the devices made with the MBE-grown structures.

6. CONCLUSIONS

6.1 Conclusion

Although CdTe has a direct, ideal band gap for solar photoconversion and a high coefficient of light absorption, optimal performance has not yet been obtained in photovoltaic applications due to grain boundaries in polycrystalline CdTe, doping issues, low minority carrier lifetime, energy barriers at contacts, and compensation from impurities⁶⁻⁹. Even after the improvements of the last several years, the highest efficiency for CdTe, as reported to date, is about 21%,¹²⁸ and the open-circuit voltage of most CdTe solar cell devices is currently less than ~860 mV,⁵⁵ lagging behind the highest GaAs thin-film solar cell efficiency of about 28.8%.¹²⁸ GaAs, a material that possess a band-gap energy nearly identical to that of CdTe, is fast approaching the maximum theoretical efficiency, which is about 32%,^{129, 130} while CdTe is still far from this maximum theoretical efficiency. The work performed during my dissertation helped to address many of the underlying problem.

At the beginning of this effort, there were serious concerns that intrinsic bulk defects would prevent solar cell improvement beyond the performance of the time. A key feature of the work performed as part of this dissertation is that the minority carrier lifetime measured for CdTe of any type – polycrystalline or single crystal – of less than 1 ns was not due to intrinsic bulk issues but was controlled almost entirely by surface passivation issues. That is, control of the surface and other interfaces is crucial to harness the potential benefits of CdTe for photovoltaic application. Admittedly, much of the initial effort in my dissertation was taken up by resolving issues specific to how we were growing CdTe and related alloy samples. Some of the relevant steps taken to control non-radiative recombination of carriers in CdTe based photovoltaic are: 1) uniform

etch/polish to prepare substrates 2) use of buffer layers that have thickness $\geq 1\mu\text{m}$ in order to limit interface recombination that might exist at the epilayer-substrate interface 3) use of $\text{Cd}_{1-x}\text{Mg}_x\text{Te}$ with x at least $\sim 0.3 \pm 0.02$ as barrier layers to clad the absorber layer in order to confine carriers and passivate the absorber layer on both sides.

After we had overcome the initial issues with our growth procedure, we were able to use CdMgTe to fabricate barrier layers, which mitigated the recombination processes at surfaces and interfaces. Along with parallel efforts by other groups,¹³¹⁻¹³⁴ we were able to show that the fundamental limitations for bulk CdTe were comparable to GaAs and not a fundamental limitation to CdTe photovoltaic performance. The background minority carrier lifetimes of $> 2\mu\text{s}$ we measured are more than sufficient to allow theoretical efficiency limits to be achieved. We also showed that the use of CdMgTe provided high quality interfaces, with interface state densities comparable to or better than that obtained for GaAs. These two results helped to reinvigorate the research being carried out on CdTe PV devices as it clearly indicated the capacity for significant improvement beyond existing performance. Mg is a useful material in the design of CdMgTe barriers for DH evaluation structures, but its practical effectiveness in real device structures is limited by the thermal diffusion of Mg atoms arising from the high temperature annealing needed to activate the p -type doping in p - n structures when dopants like As are used. It may prove a useful material for some processes, but the limitations must be clearly understood.

This research study provides a better understanding of the thermal processing limits for CdMgTe barriers and concludes that the combination of Zn alloying and lattice matching to reduce strain can decrease the rate of diffusion of Mg atoms in CdTe, expanding this study's technological relevance. Specifically, our result indicate that the

process temperature for using CdMgTe in devices should remain below 500 °C. If this can be achieved, then CdMgTe can be a viable component of a PV device structure.

One potential improvement of CdTe PV structures is to replace the front CdS *n*-type layer, which forms a heterojunction with a material with improved interface properties. Two possibilities were a heavily *n*-type CdTe homojunction, or a different II-VI emitter such as CdMgTe.

Iodine was used in this research effort to obtain *n*-type CdTe. Dopant activation of about 80% was observed in most of the iodine-doped CdTe samples and the estimated activation energy of Iodine in CdTe is about 6 meV. Carrier lifetime of $\sim 1 \mu\text{s}$ was measured in a sample that has iodine doping concentration of $\sim 1 \times 10^{15} \text{ cm}^{-3}$. When compared with indium-doped CdTe/CdMgTe DHs, at similar doping concentration, iodine-doped CdTe/CdMgTe DHs have higher carrier lifetime. The PLI comparison show that indium-doped CdTe/CdMgTe DHs at doping concentration above $5 \times 10^{16} \text{ cm}^{-3}$ start to show photoluminescence degradation, whereas iodine-doped CdTe/CdMgTe DHs does not show photoluminescence degradation at doping concentration as high as $2 \times 10^{18} \text{ cm}^{-3}$. Iodine was shown to be more thermally stable than indium at temperatures up to 600 °C. Thus, the use of I provides the option for future study of I-doped homojunction devices.

I-doping also allows technologically useful doping of *n*-type CdMgTe. For iodine-doped $\text{Cd}_{0.65}\text{Mg}_{0.35}\text{Te}$, dopant activation of about 40% was observed in samples with donor density of up to $2 \times 10^{17} \text{ cm}^{-3}$ and the activation energy of iodine in $\text{Cd}_{0.65}\text{Mg}_{0.35}\text{Te}$ is about 58 meV. Activation energy for $x \sim 0.25$ is 17 meV, while it is 20 meV for $x \sim 0.3$. The room temperature mobility was observed to be $800 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for I-doped CdTe while it was around $38 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for I-doped $\text{Cd}_{0.65}\text{Mg}_{0.35}\text{Te}$. Electrical

properties were observed to change abruptly around $x \sim 0.35$ for iodine-doped $\text{Cd}_{1-x}\text{Mg}_x\text{Te}$; although this phenomenon is not clearly understood, one possible explanation is that a deep-donor state exists and gets pushed into the band gap as x increases. The activation energy of 20 meV of iodine in $\text{Cd}_{0.7}\text{Mg}_{0.3}\text{Te}$ shows that iodine is a shallow donor in $\text{Cd}_{1-x}\text{Mg}_x\text{Te}$ with a Mg composition up to $x \sim 0.3$.

However, preliminary use of *n*-type CdMgTe suggests barrier formation as shown figure 91 (section 5.1), where the J-V characteristics of CdMgTe:I/CdZnTe:As solar cell structure show the dependence of the total current on the voltage. The barrier formation impedes hole transport, which can eventually affect device performance.

In this study, low SRV was demonstrated in undoped and I-doped DHs. I-doped DHs have a lifetime well in excess of the radiative lifetime due to the photon-recycling effect. This is consistent with what was observed for doped GaAs/AlGaAs DHs, emphasizing that, once surface recombination is controlled, the electronic properties of CdTe are comparable to those of GaAs with the potential benefits of a slightly lower radiative recombination parameter and a higher tolerance to dislocations. Iodine shows no evidence of PL degradation with doping as high as $2 \times 10^{18} \text{ cm}^{-3}$ (the highest in a DH grown to date). This result, coupled with the longer lifetimes observed for I doping and compared to equivalent In-doping levels, is a clear indicator that iodine is an efficient dopant to achieve highly doped *n*-type CdTe. In addition, iodine doping has low activation energies for technologically important barrier compositions. Iodine doping is also robust for diffusion in CdTe structures, with or without As-doping.

While surface passivation is likely the dominant limitation in CdTe PV, the next remaining issue is doping on the p-side of the device. The current p-type dopant, Cu has

many significant limitations and the consensus of the community is it should be replaced. The research described in my dissertation made two significant contributions in the potential for As to replace Cu. One significant result is that there is a distinct solubility limit for As in CdTe that limits heavy doping. This was easily seen for $[As] > 5 \times 10^{17} \text{ cm}^{-3}$ as observed in SIMS measurements where structural degradation is characterized by rapid increase in As incorporation. APT measurements consistent with SIMS measurements show As clustering in the same region where structural degradation was observed with SIMS. A lower value in the range of $5 \times 10^{16} - 1 \times 10^{17} \text{ cm}^{-3}$ may be suggested by Hall effect measurements. That is, doping in this range appears compensated which suggesting some segregation or compensation mechanism comes into play limiting *p*-type doping efficacy.

In this research endeavor, an acceptor density of $\sim 2 \times 10^{16} \text{ atoms/cm}^3$ was reproducibly achieved in MBE-grown CdTe:As and CdZnTe:As structures. Growth conditions that lead to the runaway effect are better understood and controlled. A net carrier density of $\sim 1 \times 10^{16} \text{ cm}^{-3}$, and a carrier lifetime $\sim 2 \text{ ns}$ can be reproducibly achieved in solar cell devices made with these As-doped structures. we note that the 2ns lifetime likely comes from remaining interface and surface recombination issues. This increased dopability which led to net carrier density of $\sim 10^{16} \text{ atoms/cm}^3$, contributed to the increase in open-circuit voltage. This is demonstrated with a V_{oc} of $\sim 880 \text{ mV}$ in the CdTe solar devices fabricated from this project. Although the slightly high carrier density in CdTe resulted in increased open-circuit voltage, the fill factor is slightly low ($< 60\%$) due to low carrier lifetime. This was a significant milestone. While this does not represent state of the art performance, it is not that far from state of the art just a few years back. Most

importantly, the device did not involve the use of Cu, and did not undergo a CdCl₂ treatment crucial for Cu-based devices. It does represent the first reasonable quality PV device incorporating As. Thus, this establishes the potential viability for the use of As in future technology improvements for photovoltaics.

The results from this research project suggest that the combination of high carrier density, high lifetime and low SRV is required in solar cell devices in order to achieve highly efficient CdTe solar cells. This work provides guide for theoretical modeling and further research to improve power conversion efficiency in CdTe solar cells.

6.2 Limitations and future Work

Some of the CdTe parameters pertinent to solar cell performance are comparable to GaAs as shown in Table 16 but the CdTe solar cell efficiency still lags the GaAs solar cell efficiency.

Table 16. Comparison between CdTe and GaAs parameters.

Property	CdTe	GaAs
Bandgap (eV)	1.514	1.42
Bulk Lifetime (ns)	> 2000	~14000
n-type doping (cm ⁻³)	~ 10 ¹⁹	10 ¹⁹
p-type dopants (cm ⁻³)	10 ¹⁶	10 ¹⁹
SRV (cm/s)	<100	10
Cladding layers	CdMgTe	AlGaAs, GaInP
Defect density (cm ⁻²)	10 ⁴	low
B _{rad} (cm ³ s ⁻¹)	1 - 3 x10 ⁻¹⁰	2x10 ⁻¹⁰

It is apparent that improving the bulk lifetime and the dopability of CdTe are not sufficient conditions for achieving highly efficient solar cell. As the bulk lifetime

improves, interfaces become dominant. It is important to note that interfaces, contacts and processing are critical to achieving high efficiency solar cell.

This dissertation uncovered some of the practical limits that constrain processes and manufacturing of PV devices. These practical limits and suggested future work are discussed below.

1. Valence-band barrier in CdTe/CdMgTe heterostructure.

There are some limitations associated with the use of CdMgTe as a passivation layer in CdTe/CdMgTe heterostructure. CdMgTe which forms type-I heterojunction with CdTe, has barriers in both conduction band and valence band. The barrier formed in the valence band could hamper hole transport. The J-V characteristics of CdMgTe:I/CdZnTe:As solar cell structure as shown in figure 91 (section 5.1) is suggestive of barrier to current flow. The doping of CdMgTe and the bandgap grading of CdMgTe seem to be viable design strategies to alleviate this challenge. Further studies to analyze the effectiveness of the bandgap grading and the doping of the barrier layer will be helpful in order to quantify the impact of these design strategies on the overall performance of the solar cell.

2. Iodine doping in device structures.

Iodine doping has been demonstrated as being useful for devices using evaluation structures, particularly its thermal stability at temperatures up to 600 °C. Iodine doping needs to be incorporated in real device structures and evaluated. It would be useful to evaluate its ability to replicate the success achieved with iodine-doped CdTe/CdMgTe DHs in device structures in order to become industry standard.

3. Arsenic annealing thermal budget

Anneal experiments show that anneal temperature of ≥ 500 °C is required to activate As dopants in CdTe-based structures. Also, device structures fabricated with RTP-annealed absorber layers show better performance than the structures fabricated with ampoule-annealed absorber layers. The RTP which does not use Cd overpressure is susceptible to Cd desorption at this high temperature which can lead to Cd vacancy formation. There is need to understand the mechanism responsible for poor performance of device structures fabricated with ampoule-annealed absorber layers. In addition, there is need to find a way to mitigate Cd vacancy formation in the RTP. Another consideration for the As annealing temperature is the thermal process limit of CdMgTe, which can be used as electron reflector in PV devices.

4. Back interface issues.

Back interface issues are common to polycrystalline CdTe. The hole barrier accompanying the use of CdMgTe as a barrier layer can further complicate the back interface issues thereby necessitating the need to consider other materials such as ZnTe, PbTe, and GaSb as barrier layer. There is an ongoing effort at Texas State University to look into these alternative materials.

5. CdCl₂ anneal treatment.

CdCl₂ anneal treatment are standard to increase grain size in polycrystalline CdTe. The study of the effect of CdCl₂ anneal treatment on each of the limit mentioned above will further provide understanding about how CdTe properties change with CdCl₂ treatment, especially grain size and crystalline orientation.

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