A Dissertation

entitled

Photoluminescence and Extended X-ray Absorption Fine Structure Studies on CdTe Material

by

Xiangxin Liu

Submitted as partial fulfillment of the requirements for

the degree of Doctor of Philosophy in

Physics

The University of Toledo

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Adviser: Alvin D. Compaan

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The direct-band-gap semiconductor CdTe is an important material for fabricating high efficiency, polycrystalline thin-film solar cells in a heterojunction configuration. The outstanding physical properties of this material such as its good band-gap match to the solar spectrum, ease of fabrication of stoichiometric films, and easy grain boundary passivation make it an important candidate for large area, thin-film solar cells. However, there are several poorly understood processing steps that are commonly utilized in cell fabrication. One of these is a CdCl$_2$ treatment near 400 °C in the presence of oxygen, which can improve the cell efficiency a factor of two or more.$^{1,2}$

Another factor is the role of copper in cell performance. In high performance CdS/CdTe thin-film solar cells, copper is usually included in the
fabrication of low-resistance back contacts to obtain heavy p-type doping of the absorber CdTe at the contact. However, most of the copper is not electrically active. For example, secondary ion mass spectroscopy (SIMS) on typical CdTe cells has shown Cu concentrations of $10^{19}$ atoms/cm$^3$ and even higher, although capacitance-voltage (C-V) measurements indicate typical ionized acceptor levels on the order of $10^{14}$ /cm$^3$. Thus, there is great interest in the location and role of this inactive copper in CdTe photovoltaic (PV) devices.

In this thesis, I will describe results obtained on magnetron-sputtered CdTe films that were diffused with copper following the procedure used for creating a cell back contact. Extended X-ray Absorption Fine Structure (EXAFS) measurements identified the chemical environment of the majority of the copper and show major differences depending on whether the CdTe film has been treated with chloride prior to the Cu diffusion. The EXAFS data indicate that the Cu chemistry is strongly affected by the chloride treatments -- predominantly Cu$_2$Te when Cu was diffused into the as-deposited CdTe film, but a Cu$_2$O environment when Cu was diffused after the vapor CdCl$_2$ treatment. There is also evidence that indicates this Cu$_2$O in CdCl$_2$ treated film locates mostly at interface of CdTe and Au contact and possibly also at CdTe grain boundaries. The significance for contact barrier and grain boundary passivation due to the Cu$_2$O will be discussed. Transformation of Cu$_2$O to CuO in CdCl$_2$ treated CdTe film after treatment under stressed conditions is observed, which indicates an additional degradation mechanism on the CdTe photovoltaic device.
Another convenient and powerful method to probe the material properties of an operating solar cell and to investigate the defect states in the active semiconductor material is cryogenic photoluminescence (PL). Ion Implantation, a doping method convenient in controlling doping level, was used to introduce specific dopants and uniform doping level in a thin surface layer of CdTe crystal. Monte Carlo simulations were performed before implantation to enable us to produce uniform doping by selecting the ion doping energies and doses. The lattice damage was removed by thermal annealing.

Photoluminescence of CdTe crystals doped with two elements, Cl and P were studied individually. PL spectra at 40K were excited by 488 nm or 752nm laser. Using implant densities typically of $10^{15}$, $10^{16}$, $10^{17}$, and $10^{18}$/cm$^3$, laser excitation power densities ranging over several orders of magnitude and temperature variation, I have identified band-to-band transitions, free-to-bound transitions and bound-exciton lines related to these species. Through the properties of these emission lines, the ionization energy of the Cl donor and the P acceptor in CdTe are also identified to be 53 meV and 70 meV, respectively.

In practice, these identified features of Cl impurities in CdTe crystals are beneficial to study the Cl in polycrystalline CdTe thin films. The 70 meV ionization energy of the P acceptor in CdTe makes phosphorus a good candidate to replace copper as the $p$-type dopant of CdTe in functional cells.
ACKNOWLEDGEMENTS

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Chapter 1 Thin Film CdTe Solar Cells

1.1 Introduction to Thin Film Solar Cells

The development of alternative sources of reliable, clean, abundant and affordable energy is more and more important today for national economic health and security, driven by the gradual depletion of the global supply of fossil fuels and the effects of the global warming caused by increased emissions of carbon dioxide and other heat-trapping greenhouse gases. By 2020, energy consumption by the United States is projected to increase by about 32% (White House Web site). Solar electricity (also known as photovoltaics or PV), as one of the renewable energy options, can make an important contribution to the economy of the United States and the world.

Photovoltaics – conversion of solar energy directly into electricity – holds the promise of unlimited, affordable, clean, flexibly applicable alternative and renewable energy resources. It has been estimated that PV modules covering about 110 miles by 110 miles of the land in United States, one-third the land occupied by roadways, could supply all the electricity consumed here with current conversion efficiency. Assuming a 30-year system life, 12% conversion efficiency (standard conditions) and 1700 kWh/m²/year of available sunlight energy, current multicrystalline-silicon PV-systems can provide a net gain of 26 to
29 years of pollution-free and greenhouse-gas-free electrical generation, except for about 4 years payback time for energy used in manufacturing.\(^7\)

**Figure 1-1** Development of record efficiencies of CuInSe\(_2\), CdTe and a-Si thin film solar cells.\(^8\)

Photovoltaic modules based on thin-film systems of amorphous silicon (a-Si) and its alloys, copper indium gallium diselenide (CuInGaSe\(_2\) or CIGS) and its alloys, and cadmium telluride (CdTe) on low cost substrates are promising candidates for long-range efficiency, reliability and low manufacturing cost. The commercial development of these modules is at different stages, with a-Si being the most advanced and CuInSe\(_2\) being the least advanced. This is mostly because of the mature knowledge of silicon semiconductors, abundant material resources and low-cost fabrication processes. However, for laboratory record efficiencies, the situation reverses. CuInSe\(_2\) and CdTe thin film PV technologies competed with each other for the leading position before the middle of the 90s and since then CIS took the leading position and has kept it to the present with the
highest efficiency of 19.2%, as plotted in Figure 1-1. The a-Si technology follows the other two.

### 1.1.1 Amorphous Silicon Solar Cells

Amorphous Silicon (a-Si) PV modules were the first thin-film material to provide a commercial product and until 2003 were the only thin film technology that had an impact on the overall PV markets (dominated by crystalline silicon PV modules presently). Compared with the band gap of crystalline silicon (c-Si) of 1.1 eV, a-Si offers a tunable band gap of 1.1~1.75 eV, which is controlled by the composition (mostly Ge) of the a-Si alloy. In addition, a-Si has a higher optical absorption coefficient (Figure 1-2) than c-Si in the visible range of the spectrum so the photoactive a-Si thickness can be less than 1 μm. Typical single-junction a-Si solar cells consist of a transparent conductive oxide (TCO) film (as the front contact and anti-reflection coating), a p-i-n (or n-i-p) diode structure and a metal film (as the rear contact and back reflector). Ge is also doped into the intrinsic, ‘i’, layer (absorber in the functional cells) to achieve a narrow bandgap for fabrication of triple-junction cells.

However, to a significant degree, the efficiencies of these modules have been limited by light-induced degradation in hydrogenated amorphous silicon (a-Si:H) and related materials used in the cell, which is recognized as the “Staebler-Wronski” effect. Due to the light-induced degradation, a single-junction cell can lose as much as 30% of its initial efficiency after about 1000 hours of illumination and a triple-junction module loses about 15% of its initial efficiency. Both material processing schemes and device design schemes
have been developed to improve the stabilized solar cell efficiency of a-Si solar cells, by usage of multi-bandgap multijunction devices and light-trapping (anti-reflection coating and back reflector of textured metal film). The present champion cells have stabilized efficiencies of 13.5% for triple-junction a-Si/a-SiGe:H/ a-SiGe:H (noted as the material of intrinsic layers), and champion modules have stabilized efficiencies of over 10%. The US industry is currently using two approaches to build a-Si-based PV modules: *substrate type* devices built on stainless steel foil with a covering of a textured back reflector, and *superstrate type* devices built on glass coated with TCO.

### 1.1.2 Copper Indium Gallium Diselenide Based Solar Cells

CuInSe$_2$ (CIS) and Cu(In,Ga)Se$_2$ (CIGS) photovoltaic cells are one of the most promising thin-film candidates for the advancement of solar-cell technology due to their high attained efficiency and low materials costs. However, certain issues have prevented the widespread commercialization and utilization of CIGS for the generation of power.\(^\text{11}\)

CIGS cells offer a tunable direct bandgap ranging from 1.02 eV to 1.68 eV by adjusting the ratio of In to Ga to maximize the absorption of the solar spectrum. CIS also has the highest average absorption coefficient ($\alpha > 10^5$ cm$^{-1}$) among the thin film PV materials,\(^\text{12}\) as shown in Figure 1-2, which can absorb 99% of the incoming photons within 1 μm.

A conventional CIGS solar cell is a layer stack consisting of a Mo back contact, the CIGS absorber, a thin CdS or ZnS window layer and a bilayer of intrinsic and aluminum doped zinc oxide (ZnO:Al) as the TCO front contact.
Modules can be deposited on soda-lime glass substrate, polymers, or metal foils. Efficiencies as high as 19.2% have been achieved at the lab scale at the National Renewable Energy Laboratory (NREL).\textsuperscript{13} Commercial modules made by Shell Solar (Camerillo, CA) have consistently reached efficiencies greater than 11%.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1-2.png}
\caption{Absorption coefficients of various solar cell materials, including CuInSe\textsubscript{2}, CdTe, a-Si:H, Cu\textsubscript{2}S, GaAs, CdS, Zn\textsubscript{3}P\textsubscript{2} and crystalline Si. Dotted line: the air mass (AM) 1.5 solar-emission spectrum. Among all these materials, CuInSe\textsubscript{2} has the highest absorption coefficient.\textsuperscript{13}}
\end{figure}

With a narrow bandgap of 1.02eV, CIS devices typically have an open circuit voltage ($V_{oc}$) less than 0.5 V. On the other hand, this bandgap allows CIS cells to absorb a large portion of the solar spectrum and generate a higher short circuit current ($J_{sc}$) than other thin-film solar cells. Meanwhile, this high $J_{sc}$ of CIS
cells also reduces module performance because of large active-area and series-resistance losses. Devices with low $V_{oc}$ typically suffer larger fractional losses at elevated temperature ($T = 60^\circ C$) often reached under PV module operating conditions.

The development of CIGS cells is also limited due to three primary concerns: (1) complicated and capital-intensive fabrication methods, (2) availability of core elements, particularly the $In$ supply, and (3) the toxicity of cadmium in the CdS buffer layer.

1.1.3 Cadmium Telluride Based Solar Cells

![Figure 1-3](image)

**Figure 1-3** Current-voltage and relative quantum efficiency curves for 16.4% efficient CdTe/CdS thin-film solar cell. 14

The direct-band-gap semiconductor CdTe is an important material for fabricating high efficiency, polycrystalline thin-film solar cells in a heterojunction configuration. The outstanding physical properties of this material such as its
good band-gap match to the solar spectrum, ease of fabrication of stoichiometric films, and easy grain boundary passivation make it an important candidate for large area, thin-film solar cells. Present-generation high-efficiency CdTe solar cells are based on $p$-type CdTe and $n$-type CdS using a “superstrate” device configuration. Refinements in window-layer processing and employing vapor CdCl$_2$ treatments have allowed the achievement of cells with efficiency of 16.4% having $V_{OC} = 847$ mV, $J_{SC} = 25.86$ mA/cm$^2$, and $FF$ (fill factor) = 74.5%. The J-V and quantum efficiency (QE) curves of this cell are shown in Figure 1-3.

However, there are several poorly understood processing steps that are commonly utilized in cell fabrication, as discussed in detail in the next section (1.2).

After all, some major challenges facing thin film photovoltaic device research can be summarized as:

1) Quantitative analysis of processing steps to provide information for efficient commercial scale equipment design and operation;

2) Device characterization relating the device performance to materials properties and process conditions;

3) Development of alloy materials with different bandgaps to allow improved device structures for stability and compatibility with module design;

4) improved window/heterojunction layers and contacts to improve device performance and reliability;
5) Evaluation of cell stability with respect to illumination, temperature and ambience and with respect to device and module structure.

My study in this dissertation mainly involves issue 2) – device characterization and materials properties of CdTe. In some respects, experimental results of this study also involve cell stability under stressed conditions as the issue 5).

1.2 Current Understanding of CdTe Solar Cells and Outstanding Issues

One of the poorly understood fabricating processes of CdTe cells is a CdCl$_2$ treatment near 400 °C in the presence of oxygen, a critical step needed to improve the performance of CdTe thin-film cells which can improve the cell efficiency by a factor of two or more.$^{17,18}$ In the history of thin-film CdTe cell R&D, the application of a post-deposition air-heat treatment of CdTe/CdS structures coated with a CdCl$_2$ layer was a turning point.$^{19,20}$ Combining the “CdCl$_2$ treatment” with advances in low-resistance contact formation led to the achievement in 1993 of a close-space sublimated CdTe cell with efficiency greater than 15%.$^{21}$

Today, the treatment step has been implemented in a variety of methods.$^{22}$ These include dipping the CdTe layer in a CdCl$_2$:CH$_3$OH or CdCl$_2$:H$_2$O solution followed by drying to precipitate a CdCl$_2$ film,$^{23,24}$ treatment in CdCl$_2$ vapor$^{25,26}$ or exposure to HCl or Cl$_2$ gas. Chlorine species may also be incorporated during CdTe film formation, in the form of Cl$^-$ ions in solution in an electrodeposition bath$^{27}$ or as a CdCl$_2$ component of screen printing slurry$^{28}$. 
The typical temperature range for the thermal cycle following chlorine incorporation is from 380 to 450°C, for 15 to 30 minutes which depends upon the CdTe film thickness.

Regarding the crystallite structure, the chloride treatment can promote recrystallization and grain growth in films having sub-micrometer initial CdTe crystallite size. This results in changing grain orientation from typically (111) to random orientation and grain coalescence yielding larger grain sizes.

Regarding the electronic properties, the post-deposition chloride treatment can also reduce the CdTe sheet resistance up to three orders of magnitude. It has been understood to be due to the combination of the recrystallization and creation of acceptor states. The primary electronic effect of Cl incorporation seems to be the formation of an acceptor complex with Cd vacancies. Both single-donor and double-acceptor states are expected to form, resulting in a single-acceptor state with a relatively shallow energy level (close to the band edge). More description is given in Section 3.3 and Figure 3-5. In this study, photoluminescence studies on Cl ion implanted CdTe crystals have been carried out to investigate the Cl-related impurity properties in CdTe. Doping through ion implantation benefits us with easily controlled impurity concentration and uniform distribution.

The effect of the chloride treatment on cell performance is increased output photocurrent and open-circuit voltage, and reduced shunting. It also improves the photocurrent micro-uniformity by the electronic incorporation of Cl and O species and CdS_{x}Te_{1-x} alloy formation by inter-diffusion between CdS into
CdTe during the high temperature process. The quantum efficiency (QE) of the chloride treated cells reaches ~0.82 at 788nm, while that of non-treated cells ranges only from 0.50 to 0.68. However, questions concerning O and Cl doping, and chemical reactions between CdCl₂ and CdTe still need to be addressed quantitatively. X-ray absorption fine structure (XAFS) studies, which can provide the local atomic arrangement around an element of interest, on chloride-treated CdTe film are meant to answer this question in this dissertation.

Another poorly understood factor is the role of copper in cell performance. In high performance CdS/CdTe thin-film solar cells, copper is usually included in the fabrication of low-resistance back contacts to obtain heavy p-type doping of the absorber CdTe at the contact. However, the instability of CdTe-based solar cells and modules is commonly thought to be related to the back contact, especially when copper doping is used. Also most of the copper is not electrically active. For example, secondary ion mass spectroscopy (SIMS) on typical CdTe cells has shown Cu concentrations of 10¹⁹ atoms/cm³ and even higher, although capacitance-voltage (C-V) measurements indicate typical ionized acceptor levels on the order of 10¹⁴/cm³. Thus, there is great interest in the location and role of this inactive copper in CdTe PV devices. XAFS studies of copper diffused CdTe films with and without chloride treatment are designed in this study to investigate the local structure of copper in CdTe.

Further development of a stable ohmic contact for CdTe compatible with monolithic integration technologies is still needed. New contacts and p-type doping into CdTe must be tested and a method developed to rapidly characterize
stability. A novel acceptor-species in CdTe – phosphorus was also studied in this work through photoluminescence on P implanted crystals. The phosphorus acceptor in CdTe with a shallower energy level (see Chapter 4) than the copper acceptor makes it a candidate for a $p$-type dopant as replacement for copper in CdTe cells.

In this dissertation, there will be two major parts. The first one, from Chapter 2 through Chapter 4, will be photoluminescence on ion implanted CdTe crystals and the second part, from Chapter 5 through Chapter 8, will be EXAFS on Cu doped CdTe films with and without prior CdCl$_2$ treatment. An introduction of Ion Implantation into semiconductors and the theory of PL will be given in Chapter 2. Then my work of PL studies on Cl and P implanted CdTe crystals will be discussed in Chapter 3 and 4, respectively. In Chapter 5, we will discuss the EXAFS techniques including the nature of EXAFS, experimental design and data extraction. Our EXAFS setup at the MRCAT beamline and sample preparation will be given in Chapter 6. The dramatic difference of the Cu local structure between chloride treated and non-treated CdTe films through EXAFS will be discussed in detail in Chapter 7. In Chapter 8, we will present a plausible model on the location of Cu$_2$O in the CdTe films and discuss the instability of Cu$_2$O in chloride-treated CdTe films. The significance of Cu$_2$O will be discussed too. And at the end, in Chapter 9, I will summarize the work of this dissertation and discuss further studies for the future.
Photoluminescence (PL) is a convenient and powerful method to probe the material properties of an operating solar cell and to investigate the defect states in the active semiconductor material. However, the unambiguous identification of the transitions responsible for the light emission, particularly in polycrystalline thin films, has been elusive. Partly to address this difficulty of identification, we have made a series of measurements on single crystals which have received calibrated doses of known atoms from ion implantation.

Studies on high quality CdTe crystals instead of polycrystalline films doped with single species have the advantage of avoiding complicated information which could involve emission lines from unknown species in polycrystalline CdTe. These include vacancies, lattice dislocations and impurities adsorbed on grain boundaries. Particularly, high quality CdTe crystals with low concentrations of defects and impurities provide a good starting point for the identification of impurity electronic energies.

Doping with ion implantation is a convenient way to introduce specific dopants and to introduce a uniform doping level in a thin surface layer. Monte Carlo simulations enable us to produce uniform doping by selecting the ion doping energies and doses. However, the disadvantage of ion implantation is that large numbers of defects are created, typically thousands of displacements for each
atom implanted. Therefore, all samples have been annealed before PL acquisition.

2.1 Design of Ion Implantation

Monte Carlo calculations using “SRIM” (The Stopping and Range of Ions in Matter\textsuperscript{35}) were performed before ion implantation. Three different ion kinetic energies were chosen to match the 0.347\(\mu\)m absorption length\textsuperscript{36} of the 752nm PL excitation laser in a CdTe crystal. 488nm excitation was also used for PL. The absorption length at this wavelength in CdTe is 0.091\(\mu\)m.

For a single energy implantation, the ion distribution under the crystal surface is a Gaussian function of depth, as shown by the dashed lines in Figure 2-1a which is the case of three single-energy-implants of Cl into CdTe. It is well known that the laser photon flux in material exponentially decreases as Beer’s law

\[ I = I_o \exp(-d/d_o) \]  \hspace{1cm} (2-1)

where \(d_o(\lambda) = 1/\alpha(\lambda)\) is the absorption length at the wavelength \(\lambda\) and \(\alpha(\lambda)\) is the corresponding absorption coefficient; \(I_o\) is the incident laser beam intensity. Thus during laser excitation, a major portion of the incident laser flux is absorbed near the sample surface at the leading tail of the Gaussian distribution which has a much lower dopant concentration than the peak center. This will complicate the interpretation of the PL data. Therefore I especially selected three ion energies with appropriate ratios in simulations in order to obtain a relatively uniform ion distribution vs. depth. The detailed simulation result will be discussed later for each elemental species individually, which are chlorine and phosphorus in this study. For demonstration, the simulated profiles of Cl ions in
Figure 2-1  a) Simulated Cl atom distribution profile in CdTe after (solid line) 400, 200 and 100 keV implantation with $5 \times 10^5$, $1.3 \times 10^5$ and $6 \times 10^4$ Cl ions, respectively, and (dashed line) the individual implantation with same amount of Cl ions; b) Cl atom distribution profile in CdTe after implantation with multiple energies as a), and laser beam intensity decay with depth in CdTe calculated in Beer’s law with attenuation length $0.347 \mu m$ for 752nm and $0.091 \mu m$ for 488nm.
CdTe with single-energy and multiple-energy implantation are compared in Figure 2-1a.

Implantation of single-crystal CdTe was accomplished at the Toledo Heavy Ion Accelerator Lab in the Department of Physics and Astronomy at The University of Toledo. High-quality CdTe crystals were obtained from Nikko Materials Co., Ltd and selected for studies involved in this dissertation. Low temperature PL data on the undoped Nikko CdTe wafer was obtained as a baseline (see Section 2.2).

All the implanted crystals were properly annealed before low temperature PL studies. The suitable annealing conditions to remove implantation-induced damage were determined on a Te-implanted crystalline CdTe from Keystone Crystal Co., which was doped with 880 keV Te to a dose of $1.25 \times 10^{13} \text{ cm}^{-2}$. The mean projected range of Te in CdTe at this energy is $R_p = 0.227\mu\text{m}$ with range straggling $\Delta R_p = 0.095\mu\text{m}$. (Note: the mean projected range is defined as $R_p = \sum x_i / N$, where $x_i$ is the projected range of ion “i” on the surface direction, i.e. the perpendicular distance from the surface to the end of an ion’s track, $N$ including all ions; the straggling is the square root of the variance $\Delta R_p = \sqrt{\left( \sum x_i^2 \right) / N - R_p^2}$ $= <(\Delta x_i)^2 >^{1/2}$) The average number of displacements generated by each incident ion is 7884 (vacancies/ion) from the simulation. This displacement density is comparable to the ones for Cl and P implantation. PL studies on these implanted crystals showed that among the successive 30-minute anneals at temperatures from 350°C to 425°C in a flowing N$_2$ atmosphere with flow
Figure 2-2  PL spectra of Te implanted CdTe wafer after successive 30 minute-annealing from 350 to 425°C. PL intensity of the annealing performed at 400°C recovered most which indicates best crystal re-growth.

Figure 2-3  Schematic representation of annealing process performed in a tube furnace.

rate: 1.5 SCFH, 400°C annealing allowed the PL intensity to recover the most which suggests optimized removal of the implantation-induced damage, as shown in Figure 2-2. Thirty-minute annealing in a flowing N₂ atmosphere at 400°C was then used as our standard annealing process for preparation of implanted CdTe samples. The annealing is always carried out in a glass tube using a sputtered
CdTe film on glass as a proximity cap to prevent possible CdTe sublimation, as represented in Figure 2-3. The glass tube is placed in an Electric Multiple Unit Furnace (type 70-T) by Hevi-Duty Electric Co. The temperature is measured through a K-type Omega thermocouple and controlled by an Omega CN9000A controller.

2.2 Photoluminescence in Semiconductors

2.2.1 Introduction

Photoluminescence (PL) is an important physical phenomenon used to characterize semiconductors which depicts the electronic structure of the materials while possibly revealing other important material features. In brief, PL occurs when a semiconductor absorbs light of energy higher than the bandgap. This results in the creation of electrons and holes in excess of their thermal equilibrium concentrations. After thermal relaxation, the excess electrons and holes recombine with a consequence of photon emission (radiative recombination) with lower energy than the excitation photons. The recombination is accomplished either directly (such as band-to-band recombination – electrons in the conduction band recombining with holes in the valence band) or more frequently, involving one or more intermediate states such as bound excitons and impurities or defects with an energy level inside the forbidden gap. A scheme of some possible radiative recombination processes occurring in semiconductors is provided in Figure 2-4.

We will examine in the coming sections more details of excitonic, donor-acceptor pair (DAP) and free-to-bound transitions. Characteristics such
as excitation power and temperature dependence or peak shape are significant in identification of the origin of these transitions and identification of the electronic states involved.

Figure 2-4  Schematic representation of six possible radiative recombination mechanisms in a semiconductor: 1. free excitons (FE); 2. neutral-donor- or 3. neutral-acceptor-bound excitons (D$^o$X, A$^o$X); 4. donor-acceptor pair (DAP); free-to-bound involving either 5. holes in the valence band to neutral donor or 6. electrons in the conduction band to neutral acceptor.

2.2.2  Excitonic Transitions

2.2.2.1  Free exciton

For high purity and high quality semiconductors at low temperature, we expect the photo-excited electrons and holes to be attracted to each other by
Coulombic interaction and to form excitons. Attraction between the electron in the conduction band and the holes in the valence band causes their motion to be correlated and the resultant electron-hole pair is known as an exciton. Typically excitons have been studied in two limiting cases. For strong electron-hole attraction, as in ionic crystals, the electron and the hole are tightly bound to each other within the same or nearest-neighbor unit cells. These excitons are known as Frenkel excitons. In most semiconductors, the Coulomb interaction is strongly screened by the valence electrons via the large dielectric constant, \( \kappa \), such as 10.3 in CdTe, resulting in weak binding of electrons and holes. Such excitons are known as Wannier-Mott excitons or simply as Wannier excitons.\(^{37}\) We shall be concerned with Wannier excitons only in this study because of the large \( \kappa \) of CdTe.

The properties of Wannier excitons can be calculated with the effective mass approximation\(^{38}\). Within this approximation, the electron-hole pair is considered as two particles moving with the effective masses of the conduction and valence bands, respectively. The donors and acceptors involved in the transitions studied in Section 2.2.4 and 2.2.5 can be regarded as similar to “excitons” but with infinite effective mass for the dopant ion.

Since the exciton is a two-particle state, its energy levels should be represented in a two-particle energy diagram instead of by one-electron energy levels.\(^{39}\) Thus within the effective mass approximation, the kinetic energy \( E_k \) of the exciton is related to wavevector \( K \) of the exciton center of mass (CM), with mass \( M = m_e + m_h \).
\[ E_k = \frac{\hbar^2 K^2}{2M} \]  

(2-2)

\[ E_r(\infty) = E_g \]

\[ E_r(n) = E_g + E_k - R^* \frac{1}{n^2} \]  

(2-3)

with \( R^* \) the Rydberg constant for the exciton defined as:

\[ R^* = \frac{\mu e^4}{2\hbar^2 \varepsilon_0^2} \]  

(2-4)

where \( E_k \) is the minimum energy of the continuum states, i.e., kinetic energy of the exciton CM, \( n (=1, 2, 3 \ldots) \) indicates the principal quantum number of the exciton.

**Figure 2-5** Energy-wavevector dispersion curves of a Wannier exciton showing both its bound states \( n = 1 \) to \( 3 \) and the continuum states. \( E_g \) is the bandgap and \( R^* \) the exciton binding energy. Also included is schematic diagram showing processes in which a photon is absorbed while producing a free electron-hole pair.

Then the exciton complex could be pictured as a hydrogen-like atom with energy \( E_r \) (as shown in Figure 2-5) given by:
state, $\mu$ is the reduced mass, $m_e^*$ and $m_h^*$ being the electron and the hole effective masses (which may be anisotropic), respectively:

$$\frac{1}{\mu} = \frac{1}{m_e^*} + \frac{1}{m_h^*}$$

(2-5)

### 2.2.2.2 Bound exciton

In real semiconductor materials, there are always small amounts of intrinsic defects or impurities forming donors or acceptors. Particularly in applications, semiconductors are usually intentionally doped with impurities – doped to form donors or acceptors and turn the materials into $n$ or $p$-type.

CdTe is one type of II-VI semiconductor. To form a donor in CdTe, either an element of group VII has to replace tellurium or group III replaces Cd. To form an acceptor, either cadmium has to be replaced by a group I element or tellurium by a group V element. One interesting feature of CdTe, or any II-VI semiconductor, is that it is amphoteric when a group IV element such as Ge is doped, by replacing either Cd to form a double-donor or Te to form a double-acceptor, which can provide two electrons or two holes, respectively, by each impurity. Besides dopants, defects in a crystal can also form donors or acceptors in a semiconductor, such as cadmium vacancies and tellurium vacancies in CdTe. Meanwhile, defects and dopants sometimes will attach to each other and form a new dopant complex in the semiconductor. For example, there have been a lot of studies on the A center in CdTe which is a single-acceptor complex consisting of a double-acceptor cadmium vacancy - $V_{Cd}$
and a donor such as Cl and I on the tellurium site - ClTe or ITe and it is noted as $(V_{Cd} - D_{Te})$.\textsuperscript{41,42}

These impurities can capture optically excited free excitons and form donor-bound or acceptor-bound excitons depending on which kind of impurity the exciton is bound to. When an exciton is trapped at a certain impurity, the total energy of the system is reduced and the radiative recombination of this bound exciton generates a photon with smaller energy than free-exciton recombination.

2.2.3 Phonon-Assisted Free Exciton Transitions

The phonon-assisted free exciton transitions are easily seen in the PL spectrum. It is the existence of asymmetric peaks lying in the photon energy below or beyond the 1S exciton. These peaks arise from phonon-assisted PLs. One of these processes, known as the Stokes emission process, is that an exciton annihilates and releases its energy to create a photon and a phonon (Figure 2-6a). Or in the other process - anti-Stokes emission, an exciton is annihilated as it absorbs the energy of a phonon with the emission of a photon (Figure 2-6b).\textsuperscript{43}

**Figure 2-6** Schematic presentation of (a) Stokes process in a medium in which a phonon is generated and (b) anti-Stokes process in which a phonon is absorbed.\textsuperscript{43}
After creation in the semiconductor by excitation photons, the exciton will relax its kinetic energy and is thermalized to the bottom of the band, which is the \( n = 1 \) band as described in the Free Exciton section (2.2.2.1). Technically the exciton is a boson (integer spin, since electrons have spin 1/2, holes have spin 1/2 (sometimes 3/2) and the orbital angular momentum must be integer). Therefore it should have Bose-Einstein statistics:

\[
\rho_{\text{exciton}}(\mu, T_e) = \frac{1}{e^{(\epsilon - \mu)/kT_e} - 1} \tag{2-6}
\]

where \( T_e \) is the exciton temperature, \( \epsilon \) is the exciton kinetic energy, and \( \mu \) is the chemical potential. In this case \( \mu = E_r(1) \) is the ground state energy of the free exciton which has been discussed in the Free Exciton section (2.2.2.1).

In a phonon-assisted process, \( \mu \) should include the energy shift \( E_p \) due to phonon creation (Stokes process) or annihilation (anti-Stokes process). Thus, the density of exciton states in three dimensions is

\[
\rho(\epsilon - \mu) \sim (\epsilon - \mu)^{1/2} \sim [\epsilon - (E_r(1) - E_p)]^{1/2} \tag{Stokes} \tag{2-7a}
\]

or

\[
[\epsilon - (E_r(1) + E_p)]^{1/2} \tag{anti-Stokes} \tag{2-7b}
\]

Here the probability of the phonon-assisted process is proportional to the probability that a phonon exists:

\[
\rho_{\text{phonon}}(E_p, T_L) = \frac{1}{e^{E_p/kT_L} - 1} \tag{anti-Stokes} \tag{2-8}
\]

Where \( T_L \) is the lattice temperature and \( E_p = \hbar \omega \) is the phonon energy. In the case of the Stokes process, the probability is proportional to \((n_{\text{phonon}} + 1)^4\).
Figure 2-7  Demonstration of Stokes and anti-Stokes phonon-assisted free exciton transition peak shape. The model is calculated with free exciton ground state energy $E_r(1)=1.596 \text{ (eV)}$, phonon energy $E_p = 0.021 \text{ eV}$, lattice temperature $T_L = 120 \text{ K}$, exciton temperature $T_e = 135 \text{ K}$.

Therefore, we obtain the phonon-assisted free exciton peak shape function:

for $\hbar \nu > \mu$

$$l(\hbar \nu) = A \left(1 + \frac{1}{\exp(E_p / kT_L) - 1}\right) \left(\sqrt{\hbar \nu - (E_r(1) - E_p)} \cdot \exp\left[-\frac{\hbar \nu - (E_r(1) - E_p)}{kT_e}\right]\right)$$

- Stokes process  \hspace{1cm} (2-9)

$$l(\hbar \nu) = A \frac{1}{\exp(E_p / kT_L) - 1} \left(\sqrt{\hbar \nu - (E_r(1) + E_p)} \cdot \exp\left[-\frac{\hbar \nu - (E_r(1) + E_p)}{kT_e}\right]\right)$$

- Anti-Stokes process  \hspace{1cm} (2-10)

for $\hbar \nu \leq \mu$,

$$l(\hbar \nu) = 0.$$
A demonstration of these two kinds of emission line shapes is shown in Figure 2-7.

In this study, the photon energy ranges of the PL spectra only cover the Stokes side of the phonon-assisted free exciton transition.

2.2.4 Shallow Impurities and Free-to-Bound Transitions

At temperatures for which $kT$ is near the ionization energy of shallow impurities, most of these impurities are ionized. In this case, electrons and holes move freely in the conduction and valence bands, hence band-to-band transitions dominate. On the other hand, at sufficiently low temperatures the thermal energy of carriers becomes smaller than the impurity ionization energy. Thus carriers are trapped at impurities; for example in p-type material most holes are trapped at acceptors with ionization energy $E_A$ when $kT < E_A$. Under this circumstance, free electrons in the conduction band can recombine with these trapped holes. Such transitions, involving a free carrier and its counterpart carrier bound to impurities, are known as free-to-bound transitions.

Free-to-bound emission lines provide a simple way of measuring impurity binding energies. In 1960, Eagles\(^{45}\) developed a theory to describe the free-to-bound emission line shape, which is given by:

\[
S(\omega) = A \omega^2 x^2 (1 + x)^{-4} f
\]

where

1. $A = \text{constant},$

2. $\hbar \omega = E$ (energy of emitted photon),
\[ x = \frac{m_c}{m_v E_i} \left[ E - (E_g - E_i) \right], \]

\( m_v \) (\( m_c \)) = valence (conduction) band effective masses, \( E_i \) = impurity ionization energy, and \( E_g \) = band gap. The function \( x^\frac{1}{2} (1 + x)^{-4} \) is approximately proportional to the absorption coefficient due to transitions between hydrogen-like acceptor levels and the conduction band.

and

\[ f = \exp \left( -\frac{E - (E_g - E_i)}{k T_e} \right) \]

which is the probability of occupation by an electron in a state of energy \([ E - (E_g - E_i) ]\) above the minimum of the conduction band.

Simplifying and expressing with measurable parameters gives:

\[ S(h\omega) = A' (h\omega)^2 \sqrt{C(h\omega - E_o)(1 + C(h\omega - E_o))} (1 + C(h\omega - E_o))^{-4} e^{-\frac{h\omega - E_o}{k T_e}} \]

where \( C = \frac{m_c}{m_v E_i} \), \( E_o = E_g - E_i \), and \( T_e \) is the electron temperature in the conduction band.

Meanwhile, \( \frac{\partial S(h\omega)}{\partial h\omega} = 0 \) shows that the emission peak intensity occurs at energy:

\[ E = E_g - E_i + \frac{k T_e}{2}. \]

This equation is used to estimate the ionization energy of the related impurity in this transition in our PL spectra analysis, as will be discussed in Chapters 3 and 4.
2.2.5 Donor-Acceptor-Pair Transitions

Quite often a semiconductor contains both donors and acceptors. Such material is known as compensated.\(^4^6\) Optically excited electrons and holes then can be captured by ionized donors \((D^+)\) and acceptors \((A^-)\) to produce neutral \(D^0\) and \(A^0\) centers. Some of the trapped electrons and holes will recombine radiatively as represented in equation (2-14). This process is known as a **donor-acceptor pair transition** (DAP transition), which can be represented by the process:

\[
D^0 + A^0 \rightarrow \hbar \omega + D^+ + A^-.
\]  

(2-14)

One characteristic of DAP emission is that the emission line shifts to higher energy as the intensity of excitation light is increased.\(^4^7,4^8\) For a low level of excitation, only a fraction of the donors and acceptors are excited and the recombination occurs on average between distant pairs. However, at high enough light excitation level, most donors and acceptors, and therefore closer pairs also, contribute to the recombination and their recombination rate is higher than distant ones.\(^4^9\) The closer donor-acceptor-pair emits photons with higher energy than more distant pairs due to higher Coulomb energy, and they contribute more emission since their recombination rate is higher. This shifts the spectrum to higher energy at higher excitation power. This results from the coulomb energy of the ionized donors and acceptors in the final state (see Equation (2-14)) since the energy of the emitted photon in a DAP transition is given by:

\[
h\omega = E_g - E_A - E_D + \frac{e^2}{4\pi\varepsilon_0\varepsilon R},
\]

(2-15)
2.2.6 Transition Identification in Photoluminescence Spectra

Transitions in PL spectra have different dependencies on excitation power and temperature. A study of these dependencies is a convenient method to identify the origins of transitions and significant information about the material, such as activation energies of impurities level, can be obtained.

2.2.6.1 Excitation Power Dependent PL

The low-temperature PL from II-VI and III-V compound semiconductors with good crystalline quality is dominated by near-band-edge-photoluminescence (NBEPL). It has been found in general that the luminescence intensity $I$ of the NBEPL emission lines is proportional to $L^k$, where $L$ is the excitation power of laser radiation and $1 < k < 2$ for excitonic transitions and $k < 1$ for free-to-bound ($eA^o$ or $hD^o$) and donor acceptor pair ($D^oA^o$) transitions.

In 1992, T. Schmidt and K. Lischka proposed a model for the excitation dependence of the NBEPL. Their model can explain experimentally observed features of the NBEPL power dependence, such as the variation of the excitonic PL intensity $I$ with $L^k$, where $1 < k < 2$, and the variation of $k$ for exciton emission lines when the wavelength of the exciting laser radiation is varied. Furthermore, they provide the $k$ values of the free exciton, bound exciton, and the free-to-bound transitions.

In order to study the dependence of the luminescence intensity $I$ on $L$, two distinct assumptions were used: (1) the case of constant concentrations of the neutral donors $N_{Do}$ and acceptors $N_{Ao}$, and (2) the case that $N_{Do}$ and $N_{Ao}$ depend on the laser intensity $L$. 
(1) Constant $N_{Do}$ and $N_{Ao}$

Based on this assumption, three cases were considered: (i) Only a small portion of the free electron-hole pairs form excitons and most photo-excited carriers recombine via defect states of donors and acceptors. This yields:

$$I_{FE}, I_{D^0X}, I_{A^0X} \sim L^2$$

which gives quadratic power dependence for the intensities of the free- and bound-exciton recombination. Also, in this case the free-to-bound transitions $(eA^0, hD^0)$ have a linear power dependence of intensity on power:

$$I_{hD^0} \sim N_{D^0} n \sim N_{D^0} L$$

$$I_{eA^0} \sim N_{A^0} n \sim N_{A^0} L$$

where $n$ is the electron density.

In the second case (ii) that exciton recombination dominates, $n \sim L^{0.5}$ for the steady state is obtained. The intensity of free-to-bound transitions then also depends on power as $I \sim L^{0.5}$. In the case (iii) that neither excitonic nor donor-acceptor recombination dominates, the transitions result in curved log($I$)$\sim$log($L$) plots. Details of the derivation will not be discussed in this dissertation but are available in Ref. 51.

At a very low level of excitation power $L$, the behavior of (i) is expected. As the light intensity $L$ level increases and a larger number of carriers form excitons, the system behaves as in (ii).

(2) Variation of $N_{Do}$ and $N_{Ao}$ with $L$

When $N_{Do}$ and $N_{Ao}$ depend on $L$, no simple analytic solutions can be obtained. However, the relations between the $k$ values were established.
Assuming that \( \frac{1}{T_{FE}} + \frac{1}{T_{nrFE}} \gg bN_{D^0} + cN_{A^0} \), T. Schmidt and K. Lischka\cite{51} obtained:

\[
k_{D^0,X} (L) = k_{FE} (L) + k_{D^0} (L) \tag{2-16}
\]

\[
k_{A^0,X} (L) = k_{FE} (L) + k_{A^0} (L) \tag{2-17}
\]

\[
k_{\phi A^0} (L) = k_{A^0,X} (L) - \frac{k_{FE} (L)}{2} \tag{2-18}
\]

\[
k_{hD^0} (L) = k_{D^0,X} (L) - \frac{k_{FE} (L)}{2} \tag{2-19}
\]

Assuming \( I_{D^0 A^0} \) is proportional to \( N_{D^0} \cdot N_{A^0} \), \( k \) for the DAP transition was obtained:

\[
k_{D^0 A^0} = (k_{D^0,X} - k_{FE}) + (k_{A^0,X} - k_{FE}) \tag{2-20}
\]

### 2.2.6.2 Temperature Dependent PL

#### 2.2.6.2.1 Bound Exciton Transition

Important information can also be obtained from an analysis of the temperature dependence of PL intensities. In the following discussion we will focus on bound exciton and free-to-bound transitions only.

In 1971, Bimberg \textit{et al.} \cite{52} first proposed a model for the temperature decay of bound excitons. This model assumes that the exciton complex has a ground state \( E_o \), where it is bound, and two higher states of energies \( E_1 \) and \( E_2 \), where it is dissociated, as represented in Figure 2-8. One then calculates the average number \( N_o, N_1 \) and \( N_2 \) of bound-electron-hole pairs in the states of \( E_o, E_1 \) and \( E_2 \), respectively, with a Boltzmann distribution:

\[
N_o (T) + N_1 (T) + N_2 (T) = N_G (T) \tag{2-21}
\]
\[
\frac{N_1(T)}{N_0(T)} = \frac{\alpha_1}{\alpha_0} e^{\frac{(E_1-E_0)}{kT}} \\
\frac{N_2(T)}{N_0(T)} = \frac{\alpha_2}{\alpha_0} e^{\frac{(E_2-E_0)}{kT}}
\]

where \(\alpha_0, \alpha_1\) and \(\alpha_2\) are the degeneracies of these levels.

Figure 2-8  Schematic representation of the ground state \(E_0\) and the two higher excited states \(E_1\) and \(E_2\) of a bound exciton. The exciton energies are given by \(E_n = -R'/(n^2)\) depending on the principle quantum number, \(n\), between the electron and hole.

For a temperature range not too extended, the total number of pairs within the three levels \(- N_G(T)\) is assumed to be constant, that is \(N_G(T) = N_G(0) = N_0(0)\). Combination of the above equations leads to:

\[
\frac{N_0(T)}{N_0(0)} = \frac{1}{1 + \left(\frac{\alpha_1}{\alpha_0}\right) e^{\frac{(E_1-E_0)}{kT}} + \left(\frac{\alpha_2}{\alpha_0}\right) e^{\frac{(E_2-E_0)}{kT}}}
\]

\[
= \frac{1}{1 + C_1 e^{\frac{E_1}{kT}} + C_2 e^{\frac{E_2}{kT}}}
\]

where \(C_1 = (\alpha_1/\alpha_0)\), \(C_2 = (\alpha_2/\alpha_0)\), \(E_{T1} = E_1-E_0\) and \(E_{T2} = E_2-E_0\).

The intensity of the radiative recombination is proportional to \(N_0(T)\), the number of electron-hole pairs in the ground state which is still available for the
process. As a consequence of neglecting any change in the radiative transition probability, we obtain the temperature dependence of the bound-exciton complex transition:

$$I(T) = \frac{I(0)}{1 + C_1 e^{\frac{E_{T1}}{kT}} + C_2 e^{\frac{E_{T2}}{kT}}}$$  \hspace{1cm} (2-25)

However, the energy level of a bound exciton may be more complex than the hydrogen-like model as proposed in Figure 2-8. For instance, for the system of an exciton bound to a neutral acceptor \((A^0, X)\) there are four possible dissociation processes\(^{54}\) resulting in four different dissociation energies \(E_{a, b, c, d}\):

a) Dissociation resulting in a free exciton:

\((A^0, X) \rightarrow A^0 + X, \quad E_a = E_B\)  \hspace{1cm} (the binding energy of the exciton to the neutral acceptor).

b) Dissociation resulting in one free electron and one free hole:

\((A^0, X) \rightarrow A^0 + e+ h, \quad E_b = E_B + E_X\)

This energy can be obtained from the energy of the photon emission from the recombination of the bound exciton:

\(h\nu_{\text{bound exciton}} = E_g - (E_B + E_X)\)

Here \(E_X\) is the binding energy of the free exciton. Thus the dissociation energy of this process includes the dissociation energies of both exciton to neutral acceptor and free exciton.

c) Dissociation resulting in one free hole:

\((A^0, X) \rightarrow (A^-, X) + h, \quad E_c = E_B - E_X\)

\(h\nu_{\text{free exciton}} = E_g - (E_B - E_X)\)
\[ E_c = E_B + E_X - E_{(A', e)} = E_B - E_{(A', e)}. \]

d) Dissociation resulting in two free holes and one free electron:

\[ (A^0, X) \rightarrow A^- + h + h + e, \]

\[ E_d = E_b + E_A \]

where \( E_A \) is the ionization energy of the acceptor.

For donor-acceptor-pair transitions the same two-activation-energy model is also applicable for the temperature dependent intensity. The activation energies are then, respectively, the ionization energies of donor and acceptor states involved in the transition.

### 2.2.6.2.2 Free-to-Bound Transitions

The PL intensity dependence of free-to-bound transitions upon the sample temperature provides another method to determine the ionization energy of the acceptor, besides measuring the peak position. For high temperatures, as \( kT \) becomes comparable to the ionization energy of the impurity, trapped carriers can jump from the impurity site into the continuum band (valence band for hole trapped in acceptor or conduction band for electron in donor). The remaining impurity will then be charged. For example if the impurity is an acceptor, then after the trapped hole is ionized to the valence band, the acceptor is left negatively charged. This ionized acceptor will not be available for electron transitions from the conduction band. Therefore, at high temperature the free-to-bound transition becomes less likely and leads to a decrease of PL intensity.
Figure 2-9  Schematic representation of free-to-bound transition.  At non-zero temperature $T \neq 0$, there are always partial occupancy of carriers (electrons in donor or holes in acceptors) thermally ionized to conduction or valence band.  Only the remaining neutral donors or acceptors are available for free-to-bound transition.

For free-to-bound transitions, the temperature dependence of intensity depends upon the available amount of impurity-bound-carriers that are the neutral impurity.  For example, for the conduction-to-acceptor transitions, the intensity depends on the amount of neutral acceptors.  A derivation similar to the previous section (the two-activation-energy model) can be readily done.  Since the total amount of acceptors ($N_A$) is the sum of neutral and ionized acceptors ($N_A^0$ and $N_A^+$) and independent of temperature, there are relationships:

$$N_{A^0}(T) + N_{A^+}(T) = N_A(T)$$

$$\frac{N_{A^+}(T)}{N_{A^0}(T)} = C \cdot \exp\left(-\frac{E_A}{KT}\right)$$

and

$$\frac{N_{A^0}(T)}{N_A(T)} = \frac{1}{1 + C \cdot \exp\left(-\frac{E_A}{KT}\right)}$$

(2-26)
There is no ionization of acceptors at $T = 0 \, K$, therefore $N_A(T) = N_A^o(0)$. Thus the temperature dependence of the conduction-to-acceptor transition luminescence intensity is:

$$\frac{I(T)}{I(0)} = \frac{1}{1 + C \cdot \exp\left(-\frac{E_A}{kT}\right)}$$

(2-27)

where $I(0)$ is the emission intensity at $T = 0 \, K$. In practice, $I(0)$ is just a constant in fitting. As to the valence-to-donor transition, the activation energy of acceptor $E_A$ then should be replaced with the one of donor $E_D$. The plot of $\log \left[ \frac{I_{PL}}{I_o} \right]$ versus $1/(kT)$ is known as an Arrhenius plot. The slope of the high temperature end of the curve will provide the ionization energy of the impurity.

However it has been discovered by Bryant$^{53}$ that in CdTe the conduction-band-to-cadmium-vacancy, $V_{Cd}$, acceptor transition (peak position at 1.554eV) intensity increases initially at low temperature when the corresponding acceptor bound exciton (1.587eV) is present as a strong emission. A similar behavior is also observed in the PL of P and Cl doped crystals as we will discuss in Chapters 3 and 4. This has been understood in the following way: At the initially low temperature, part of the neutral acceptors provide a trap center for the free exciton and the neutral acceptors are screened by the bound excitons; when the temperature increases, an Auger process occurs for the dissociation of the exciton-neutral acceptor state then resulting in the ground state available for conduction-to-acceptor emission:

$$ (V_{Cd})(e,h) \rightarrow (V_{Cd}) + (e,h)$$

(2-28).
The activation energy of the dissociation process was estimated to be around 2meV.

### 2.2.7 PL Experimental Set-up

The photoluminescence was detected by a Jobin-Yvon S3000 monochromator system. This system consists of two main components which are the DHR 320 double monochromator which acts as a filter and the HR 640 monochromator. The detailed description on the setups of these two monochromators has been discussed before in Dan Grecu’s PhD dissertation in 1999. In order to increase the PL signal intensity reaching the CCD detector, the DHR 320 monochromator which works as pre-filter was taken off recently. The temperature-dependent PL data of all the samples in this study and the PL of phosphorus-implanted samples were taken without the pre-filter. The entrance silt for the HR 640 (without the DHR 320 pre-filter) was set to 65μm for measurements in this study.

The spectrometer was used in conjunction with a Princeton Instruments CCD detector with 1152 x 298 pixels operating at -110°C, cooled by liquid nitrogen. The theoretical instrumental resolution is around 2.5Å which is in good agreement with the approximate 5Å experimental full width at half-maximum observed for a Kr gas discharge spectrum.

The wavelength calibration was performed using the emission lines of a Kr gas discharge lamp. Details have been represented in Dan Grecu’s dissertation and the same method was employed in this study. The system was calibrated and corrected for the CCD/spectrometer response. A new
calibration was performed after the DHR 320 pre-filter was removed, as shown in Figure 2-10.

![Figure 2-10](image-url) Detection efficiency of the spectrometer/CCD system for HR640 set at the near-band-edge range of CdTe.

The samples were mounted in a Leybold closed-cycle He refrigerator capable of operating at temperatures as low as 10K. A Lake Shore DRC-91CA temperature controller is used to adjust the temperature. During the spring of 2005, it was discovered by Levi Gorrell that the minimum sample temperature was actually approximately 40K with the thermometer reading of 10K. Levi improved the sample cooling by polishing the surface of the copper cold finger and moved the thermometer lower onto the tip of the cold finger closer to the sample location. A homemade thermal paste consisting of APIEZON N and copper powder with a volume ratio of 2:1 is employed for sample mounting. The lower temperature readout of the thermometer has been calibrated with the ruby
R₂ and R₁ line emission intensity ratio, \( I₂/I₁ \), which has a relationship with temperature as \( I₂/I₁ = \eta \exp(-\Delta/KT) \) as proposed by Weinstein. For this calibration, a ruby crystal chip was mounted beside the CdTe samples during PL data collection. The same homemade thermal paste was applied to mount the ruby crystal and CdTe wafers to the copper colder finger of the He refrigerator. The quantum efficiency ratio of the \( R₂ \) to \( R₁ \) transition - \( \eta \) was calibrated at 77K by immersing the ruby crystal in liquid nitrogen with detection by an optical fiber. Our calibrated \( \eta \) value is 0.773 instead of 0.65 provided by Weinstein. The lower temperature ruby crystal calibration with this \( \eta \) value is in good agreement with the thermometer reading as listed in Table 2-1. A better sample cooling has been established. The lowest sample temperature reaches as low as 9K.

### Table 2-1 Thermometer measurement and ruby crystal temperature calibration.

<table>
<thead>
<tr>
<th>Thermometer T (K)</th>
<th>Ruby XTAL Calibration (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.6</td>
<td>9.92 ± 0.095</td>
</tr>
<tr>
<td>11.0</td>
<td>12.18 ± 0.098</td>
</tr>
<tr>
<td>12.0</td>
<td>13.33 ± 0.10</td>
</tr>
<tr>
<td>14.0</td>
<td>15.00 ± 0.10</td>
</tr>
<tr>
<td>16.0</td>
<td>17.01 ± 0.11</td>
</tr>
<tr>
<td>20.02</td>
<td>20.76 ± 0.14</td>
</tr>
<tr>
<td>24.03</td>
<td>24.81 ± 0.16</td>
</tr>
<tr>
<td>27.15</td>
<td>28.23 ± 0.20</td>
</tr>
<tr>
<td>30.17</td>
<td>31.39 ± 0.23</td>
</tr>
</tbody>
</table>

The PL was excited with the 752.5nm (1.6476 eV) radiation of a Kr⁺ ion laser and with the 488nm (2.5406 eV) line of an Ar⁺ laser. Excitation powers
ranging between 0.5μW and 5mW were achieved by the use of neutral density filters. The laser was focused on the sample using spherical optics to a diameter of 100 ~ 120μm. An incident power of 5mW focused on the sample in a 100μm diameter spot results in an energy density equivalent to approximately 640 suns. (1 sun = 1 AM1.5 = 100mW/cm²) The photoluminescence photons were collected by a camera lens with focusing length f = 13.5cm and aperture size f/2.8 and then focused into the grating system. The experimental arrangement is schematically plotted in Figure 2-11.

Figure 2-11  Schematic representation of optics arrangement of PL excitation and collection.

2.2.8  Instrumental Broadening

Here we shall discuss a practical topic in spectroscopy measurements – instrumental broadening, since this is involved in all of our PL spectra.

Convolution, in its simplest form, is usually considered to be a blurring or smoothing operation. A “bumpy” function, such as the real emission lines of
free-to-bound and phonon-assisted free exciton, is convolved with a smoothing function to yield a smoother output (collected PL spectra in our case). Ideally, the response function of a CCD detector to a photon at each single wavelength $\lambda$ should be a delta function $\delta(\lambda)$. However, in practice, the slit width of the spectrometer entrance is finite and the image of the entrance onto the CCD is usually wider than the size of the CCD elements. Therefore, the response function of the CCD is always a broadened delta function and the collected PL spectrum by a CCD is a result of convolution of this broadened delta function and the real spectrum.

If the spectrometer has a broadening response function $b(u)$, then the collected data $a(u)$ of the ideal photoluminescence spectrum $g(u)$ can be expressed as:

$$a(u) = \int_{-\infty}^{\infty} b(u - u') g(u') du'$$

(2-29)

If the area under response function $b(u)$ is unity,

$$\int_{-\infty}^{\infty} b(u) du = 1$$

(2-30), we may say that $b(u)$ is normalized. Equation (2-29), represents a moving weighted average. In the instrumental resolution study, we often think of the convolution integral in this way.

However, in a real spectrometer, data are collected as a discrete function. Then the instrumental broadening effect should be:

$$a_n = \sum_{m=-\infty}^{\infty} b_{n-m} g_m$$

(2-31)
In this dissertation, the author collected the broadening response function \( b(\nu) \) from atomic emission lines, which are effectively single wavelength transitions. Then I normalized the measured response function by applying:

\[
B(\nu) = \frac{b(\nu)}{\sum_{\nu' = \nu_1}^{\nu_2} b(\nu') \cdot \Delta \nu'}
\]

(2-32)

where \( \nu_1 \) and \( \nu_2 \) are the lower and upper photon frequency limits, respectively, of the measurement range. Convolution of the PL model with the normalized response function \( B(\nu) \) according to equation (2-31) is then fitted to the experimental spectra to obtain the corresponding physical parameter of each transition in PL. A typical normalized response function is shown Figure 2-12.

![Normalized response function](image)

**Figure 2-12** A normalized broadening response function transformed from one emission line of the Kr lamp. Data were collected with the 298x1152 pixels CCD detector.

### 2.3 Single Crystal CdTe

In the last two years, we received two pieces of high quality CdTe crystals (wafers) from Nikko Material Co. Figure 2-13 illustrates a typical PL
spectrum of a CdTe single crystal supplied by Nikko Material Co. (which is noted as 2nd quality as described later), at 40 K excited with 488nm (2.5406 eV) from an Ar laser at two photo-excitation powers. The band gap of CdTe at this temperature is approximately 1.604eV.58

**Figure 2-13** Typical PL spectrum of single CdTe crystal (2nd quality) excited by 488nm laser with 10 and 500 W/cm². The sample was cooled down to 40 K. Indicated on the figure are the free exciton (FX), bound exciton (BE), phonon assisted free-exciton (FX-1LO), free-to-bound (FB), the phonon replica of free-to-bound (FB-1LO), and “defects” band.

Three main regions can be distinguished in the spectrum: transitions between 1.57 and 1.61eV are generally attributed to exciton transitions; transitions between 1.51 eV - 1.57eV are typically assigned to free-to-bound transitions and their phonon replicas; transitions between 1.35 – 1.50eV are typically attributed to donor-acceptor pair (DAP) transitions involving deeper defect states.

Figure 2-14 shows the PL from the other one of the undoped CdTe wafers from Nikko Materials Co., Ltd, which exhibits extremely low defect-associated photoluminescence. This will be noted as “first quality.” The normally broad
defect band at 1.44 eV is not observed on this wafer. Meanwhile a series of peaks around 1.59 eV related to bound-exciton emission and around 1.575 eV, identified later to be the phonon-assisted free exciton transition are observed that overwhelm other features. This indicates very low transition rates of nonradiative recombinations in the crystal, which transfers the energy of excited electron-hole pairs into phonons. The non-radiative recombination occurs in semiconductor crystals usually with the assistance of shallow defects. Thus a low concentration of defects, such as lattice dislocations and residual impurities, is expected in this crystal.

Figure 2-14  PL from the 1st quality and 2nd quality CdTe wafers supplied by Nikko Material Co. (noted as NM) as well as CdTe wafers from Keystone Crystal Co. (noted as KC). All of the PL spectra were excited by a 752nm laser beam with the same focus. Samples were cooled down to 40 K.

Even though, on the other wafer supplied by Nikko ("second quality"), we observed substantial intensity of defect bands, the exciton-related peaks still dominate other features in the spectra. The origin of the defect bands in the 2nd
quality crystal can be explained by residual Cl impurities as identified later in Chapter 3 (Section 3.3). Compared to either wafer from Nikko Materials, the PL of the CdTe wafer supplied by Keystone Crystal Co. (our previous supplier) has the excitonic band with intensity almost one order of magnitude lower. This suggests more non-radiative recombination centers capturing optically excited electron hole pairs, which compete with radiative recombination and reduce the luminescence intensity. The concentrations of residual lattice defects in the crystals are the most plausible origin of this difference between the wafers from different suppliers. For the purpose of PL studies, both first and second quality Nikko Materials CdTe wafers were selected for the ion implantation involved in this dissertation.
Chapter 3 Photoluminescence Identification of Chlorine Dopants in CdTe Single Crystals

3.1 Introduction

As mentioned in Chapter 1, high-temperature CdCl$_2$ treatment in the presence of oxygen is a critical step needed to improve the performance of CdTe thin-film cells, which can improve the cell efficiency a factor of two or more.$^{60}$

![Figure 3-1](attachment:image.png)  
**Figure 3-1** Representation of complete cell structure fabricated by the UT CdTe PV group.$^{61}$ This is a typical superstrate structure in which the glass substrate is the first layer sunlight reach in operation.

At the University of Toledo, our CdTe PV group uses a high temperature CdCl$_2$ vapor process for the chloride treatment on CdTe in cell fabrication. This process is performed at 387°C in a CdCl$_2$ vapor environment for 30 minutes, with dry air (<10PPM water) flowing for 1 minute at 1 sccm every 19 minutes during the 30 minutes annealing and initial 35 minutes of heat up and the following
cooling period. It actually takes approximately 1 hour and 30 minutes for the system to cool down to room temperature. This process was developed following McCandless\(^2\) to optimize the performance of cells with 0.13\(\mu\)m CdS/2.3\(\mu\)m CdTe superstrate structure on soda-lime glass substrates coated with a transparent conducting oxide, usually SnO\(_2\):F. The cells then receive thermally evaporated Cu (35\(\AA\)) and gold (200\(\AA\)) films followed with diffusion at 150 °C in ambient air for 45 minutes. All of these values are given for standard UT CdTe

![Figure 3-2 UT CdTe I-V and quantum efficiency characteristics tested at the National Renewable Energy Lab (NREL). The I-V was measured under one-sun illumination.61](image)
cells. The complete cell structure is represented in Figure 3-1. The typical cell performance with this structure is $V_{OC} \sim 820$ mV, $J_{SC} \sim 20mA/cm^2$, FF > 70% and 12~13% efficiency, as shown in Figure 3-2. All the $CdCl_2$ treatment, or simply chloride treatment as quoted in this dissertation, shall only mean this $CdCl_2$ vapor treatment described above.

As we discussed in Chapter 1, even though the chloride treatment is a critical step to improve the performance of a CdTe cell and has been empirically optimized for different CdTe deposition methods, the mechanism of the chlorine treatment effect on CdTe is still poorly understood. The thin film PV community has great interest in the nature of the electronic property changes due to the chlorine treatment. In this chapter, we shall focus on the electronic structure of Cl-implanted CdTe crystals revealed by low temperature photoluminescence.

### 3.2 Sample preparation

As shown in Chapter 2, Figure 2-1, three Cl ion kinetic energies were chosen for the ion implantation into both first quality and second quality NM CdTe wafers. The three Cl ion energies are, respectively, 400, 200 and 100 keV. To achieve a final uniform Cl profile below the wafer surface, the author selected 72.46, 18.84 and 8.70% of total ion amount for the three energies, respectively, based on a Monte Carlo simulation by SRIM. The ion concentration profile generated by SRIM has been plotted in Figure 2-1. The projected range $R_p$ and the range straggling $\Delta R_p$ from the simulation are, respectively, 0.277 and 0.152 μm. The average amount of vacancies generated by ion bombardment is 2004
Vacancies/ion. The simulation results for the triple-energy implantation and the three single-energy implantations have been summarized in Table 3-1.

<table>
<thead>
<tr>
<th>Energy (keV)</th>
<th>( R_p(\mu m) )</th>
<th>( \Delta R_p(\mu m) )</th>
<th>Vacancies/ion</th>
<th>Fraction of Doses(%)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.3316</td>
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<td>2004</td>
<td>100</td>
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</tbody>
</table>

The Cl species implanted into the crystals are then assumed to be uniformly distributed from the surface to a depth of \( R_p + \Delta R_p \) to compute the total ions to be implanted into the crystal for designed Cl concentrations. CdTe wafers were cut from the same piece to avoid any crystal structure or impurity variations. Sodium Chloride powder as the ion source for implantation was thermally vaporized and ionized by an electron beam in the high vacuum chamber of the accelerator. The 2\(^{nd}\) quality NM crystal was implanted with four different Cl concentrations: \( 3 \times 10^{16}, 1 \times 10^{17}, 1 \times 10^{18}, 1 \times 10^{19} \) \((1/cm^3)\). One piece of the 1st quality NM crystal was also implanted with \( 3 \times 10^{16} \) \((1/cm^3)\) Cl. Due to the limitation of the size of crystals provide by Nikko Materials Co., only one implantation concentration was made on this high quality crystal. Standard annealing, described in Chapter 2, was carried out on all of the implanted wafers before PL acquisition.
3.3 Cl in the High Quality Crystal

Figure 3-3 PL of pure 1st quality NM CdTe wafer without any intentional doping and treatment, and Cl implanted same wafer with concentration $3 \times 10^{16} \text{ (cm}^{-3}\text{)}$. Both were excited by 50W/cm$^2$ 488nm laser beam.57

Taking advantage of the 1$^{st}$ quality NM crystal, we implanted one piece with $3 \times 10^{16} \text{ (cm}^{-3}\text{)}$ Cl. The most obvious change of the spectrum after Cl...
implantation is that the intensity of the whole spectrum, including the exciton band, free-to-bound and defect band emissions increases dramatically, as demonstrated in Figure 3-3. The intensity of the exciton band, including the bound exciton and FX-1LO, increased by a factor of about 10 after Cl implantation, and a defect band appears. This demonstrates a substantial passivation of non-radiative recombination centers. Besides the intensity increasing, a new free-to-bound transition peaking at 1.553 eV appears that was not present in the undoped sample.

![Graph](image)

**Figure 3-4** Computed FX-1LO transition line shape and experimental PL data of 3x10^{-16} (cm^{-3}) Cl implanted CdTe.

A strong shoulder at 1.575 eV is observed (Figure 3-3b), which arises from phonon-assisted free-exciton emission. The peak shape can be fitted with the model described in Chapter 2 combined with a convolution of the spectrometer broadening response function. As shown in Figure 3-4, the dashed line is the calculated peak shape. In the computation, the transition
threshold is set to be 1.574 eV, the crystal temperature is $T_L = 45 \pm 1$ K and the electron temperature is $T_e = 53 \pm 1$ K. Given the phonon energy in CdTe of 0.021 eV, the corresponding free exciton energy would be at 1.595 eV. In the PL spectrum of the Cl-implanted sample, a shoulder at around this energy can be identified but it is overlapped by the strong bound-exciton peak. However, in the spectrum of the undoped first quality crystal, a sharp transition line peaking at 1.596 eV is identified. The difference could arise from the strong bound exciton peak on the lower energy side of the FX line which pushes the peak position to higher energy. Using the effective masses of electrons in the conduction band $m_e = 0.09$ and holes in the valence band $m_h = 0.41$, and the dielectric constant of CdTe as $\varepsilon = 10.6$, the ground energy state of the (hydrogenic) FX in CdTe is

$$R^* = 13.6 \times \frac{\mu}{\varepsilon^2} \text{(eV)} = 0.0089 \text{(eV)}$$ below the band gap. Thus the band gap can be speculated to be $E_g = E_r(1) + R^* = 1.604$ eV at 45K. This value is in good agreement with G. Fonthal et al.'s work on the temperature dependence of the CdTe band gap.

The neutral-donor-bound exciton emission at 1.591 eV from the Cl-implanted wafer has intensity 15 times that of the undoped crystal (Figure 3-3). This recombination of excitons bound to shallow neutral donors ($D^0X$) has also been identified by T. Schmidt.$^{65}$ We suggest the neutral donor in our sample is the defect of Cl substituting on a Te site - Cl$_{Te}$. That the peak appears strong in Cl-implanted crystals but weak in undoped ones indicates the existence of some residual Cl impurities in the NM CdTe wafer.
The emission line at 1.549 eV appears in both Cl-implanted and undoped crystals with approximately the same intensity and with the same asymmetrical shape. This indicates it is a free-to-bound transition arising from a residual impurity in the crystal. We are not able to identify the origin of the impurity contributing to this 1.549 eV transition. However it is clearly not related to the Cl implantation.

The transition at 1.553 eV appears in the Cl-implanted wafer but is not observed in the undoped crystal. This suggests it is a chlorine-impurity-related transition. We have identified it as a free-to-bound transition by fitting the line shape to the model described in Chapter 2. Due to the much weaker intensity of this peak than the exciton band and strong nearby tail of the exciton band, a fitting to this line is unreliable. Fortunately, in Cl-implanted 2nd quality NM wafers, strong transitions appear and we carried out fitting to those spectra. These will be discussed in the coming section.

Even though fitting this spectrum is not possible, with the peak energy $E_{\text{peak}} = 1.5529 \, (\pm 0.0002) \text{ eV}$, we are still able to estimate the ionization energy of the Cl-related impurity to be $E_i = E_g - E_{\text{peak}} + K T_e / 2 = 53.0 \, (\pm 0.2) \text{ meV}$ by using the hole temperature $T_h \equiv T_L = 45 \, (\pm 1) \text{ K}$ and bandgap energy $E_g = 1.604 \text{ eV}$ inferred from the FX-1LO transition.

One could argue that this transition is either a free-to-bound transition related to chlorine donor at a tellurium site $\text{Cl}_{\text{Te}}$ or an A-center acceptor ($\text{V}_{\text{Cd}} - \text{Cl}_{\text{Te}}$) as the complex of cadmium vacancy (double acceptor) and chlorine donor $\text{Cl}_{\text{Te}}$ (single donor), which is schematically represented in Figure 3-5. The electron
binding energy of the Cl donor in CdTe ($\text{Cl}_{\text{Te}}$) has been identified to be 14 meV by D. M. Hofmann$^{66}$ et al. by optically detected magnetic-resonance (ODMR). However this value does not match our observation. They observed a DAP transition between the Cl donor and the A-center acceptor and calculated the hole binding energy to the A center to be $120 \pm 3$ meV. These values cannot explain our observation either. I will provide our interpretation to this free-to-bound transition in my discussion on the power-dependent study of this free-to-bound transition in Section 3.5.3 and 3.7.

Figure 3-5  Schematic representation of $\text{Cl}_{\text{Te}}$ donor and A-center ($V_{\text{Cd}}$-$\text{Cl}_{\text{Te}}$) in CdTe.

The DAP transition between the Cl donor and the A-center acceptor at 1.478 eV and the corresponding LO-phonon replicas identified by Hofmann,$^{66}$

$$D^0 + A^0 \rightarrow D^+ + A^-$$

$$\text{Cl}^0 + (V_{\text{Cd}} - \text{Cl}_{\text{Te}})^0 \rightarrow \text{Cl}^+ + (V_{\text{Cd}} - \text{Cl}_{\text{Te}})^-,$$
are also observed in our Cl-implanted wafer. This confirms the existence of both the Cl donor and the A center (V_{cd} - Cl_{Te}) complex in the CdTe crystal after Cl implantation.

3.4 Cl Dose Dependence

Figure 3-6 The PL spectra of Cl-implanted CdTe with four concentrations and the undoped crystal: a) whole spectrum range; b) expanded scale in the excitonic range. PLs were excited at 752nm with 5W/cm^2. Samples were cooled down to around 40K.

To accomplish the understanding of the Cl concentration effect on the impurity energy levels, we implanted the 2^{nd} quality NM CdTe wafer with four
medium-level doses – $3 \times 10^{16}$, $1 \times 10^{17}$, $1 \times 10^{18}$, $1 \times 10^{19}$ (cm$^{-3}$). Examples of PL spectra of these samples and the undoped NM crystal are plotted in Figure 3-6. As shown in the figure, the free-to-bound (1.556 eV), phonon-assisted free-exciton (FX-1LO at 1.575 eV), bound exciton (~1.590 eV), and the defect band emissions all intensify after Cl implantation just as in the 1$^{st}$ quality wafer. And the intensities increase with Cl concentration in the crystal.

**Table 3-2** The red shift of D$^0$X peaks with Cl concentration.

<table>
<thead>
<tr>
<th>Cl concentration(cm$^{-3}$)</th>
<th>D$^0$X peak position (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3 \times 10^{16}$</td>
<td>1.5915 ± 0.0002</td>
</tr>
<tr>
<td>$1 \times 10^{17}$</td>
<td>1.5908 ± 0.0002</td>
</tr>
<tr>
<td>$1 \times 10^{18}$</td>
<td>1.5899 ± 0.0002</td>
</tr>
<tr>
<td>$1 \times 10^{19}$</td>
<td>1.5888 ± 0.0002</td>
</tr>
</tbody>
</table>

Meanwhile, we observed a red shift of the bound-exciton emission peak (~1.590 eV) as the Cl concentration increased, as shown in Figure 3-6 and summarized in Table 3-2. This is because the bound exciton emission shifts with increasing Cl concentration from the D$^0$X line at 1.591 eV to A$^0$X emission at 1.589 eV.$^{51}$ Since Cl should always act as a donor in CdTe, the overwhelming acceptor concentration in heavily doped samples can only be explained by the formation of A center complexes. Compensation is also observed through the DAP transition at 1.478 eV and its series LO-phonon replicas (Figure 3-6a and refer to Figure 3-3a). The 1.478 eV DAP line arises as a transition between the Cl donor and the Cl A-center as identified by Hofmann. Intensities of these
series peaks keep increasing with Cl dopant concentration, and particularly get enhanced when the Cl concentration exceeds $1 \times 10^{18} \text{ cm}^{-3}$ which suggests a dramatic increase of the number of A-centers. This may be due to a large amount of cadmium vacancies left by insufficient annealing of implantation-induced damage.

The broad band of the $1 \times 10^{19} \text{ cm}^{-3}$ sample at around 1.54 eV suggests insufficient annealing for this high dose implantation. Thus we will not discuss more details on this sample except for the $D^0X$ peak.

3.5 Excitation-Power-Dependent PL

3.5.1 Exciton Emissions

In Figure 3-7, the four panels plot excitation-power-dependent PL in the excitonic band region of the standard annealed NM CdTe crystal with no-intentional doping and with the three different Cl concentrations in the crystal. For convenience of comparison, spectra of lower powers are multiplied by certain factors except for the highest one 50W/cm$^2$. (Note: in this power dependent PL study, the laser beam was focused onto the surface of the crystal; the focal spot size was determined to be 100~120 μm, or area ~$8 \times 10^{-5} \text{ cm}^2$, by scanning a 10 μm pinhole across the focal spot at the plane of the sample surface.) To extract the intensity of the Cl-neutral-donor-bound exciton emission line, a multiple curve fitting was performed. Since there are strong free-to-bound and FX-1LO emissions which overlap with the bound exciton lines, as shown in Figure 3-8a), I established a computer code combining the free-to-bound emission line shape model from Eagles (Section 2.2.4), phonon-assisted free-exciton (FX-1LO) on
Figure 3-7  Excitation-power-dependent PL in the excitonic region: a) undoped standard annealed 2\textsuperscript{nd} quality NM crystal; b) CdTe:Cl 3\times10^{16} \text{(cm}\textsuperscript{-2})\text{; c) CdTe:Cl 1\times10^{17} \text{(cm}\textsuperscript{-3})\text{; d) CdTe:Cl 1\times10^{18} \text{(cm}\textsuperscript{-3})}. PLs were excited by the 488nm Ar laser. Samples were cooled to around 40K.

the Stokes side (Section 2.2.3) and convolution of these two models with the instrumental broadening response function (Section 2.2.8), as described in Chapter 2. One representation of this computed model best fitting to our data of 3\times10^{16} \text{(cm}\textsuperscript{2}) Cl in CdTe is plotted in Figure 3-8a. The excitonic band intensity is extracted (Figure 3-8b) then for multi-curve fitting by the Peak Fitting Module v 7.0 in Origin\textsuperscript{67}. 


The best fit results in four Lorentzian peaks centered at $1590.48 \pm 0.08$, $1592.25 \pm 0.1$, $1595.96 \pm 0.6$ and $1600 \pm 2$ meV. The two peaks at $1.596$ and $1.600$ eV are emissions of the ground state and first excited state of free excitons within the error range, since $R^* = 8.9$ meV (Section 3.3) for CdTe and the energy
difference of these two states should be \( R' \times (3/4) = 6.7 \text{ meV} \). The peak at 1.59225 eV has been observed in the undoped crystal (Figure 3-6) as a bound exciton of certain unidentified residual impurity. The peak at 1.5905 eV is the Cl donor bound exciton emission.

We found the bound exciton emission lines can be fitted very well with a Lorentzian shape. This can be understood as the homogeneous line-broadening originating from the variation of band edges of conduction and valence bands.

![Figure 3-9](image)

**Figure 3-9** Log(\( I \)) vs. log(\( L \)) of the undoped and Cl-implanted 2nd quality NM crystal with three concentrations. \( I \) is the intensity of the 1.5905 eV Cl donor bound exciton line. \( L \) is the laser power. Fittings to the \( I \sim L^k \) law are plotted with the four dashed lines.

Coming back to the intensity of the Cl-donor-bound exciton, similar extractions of the intensity and multi-curve fitting were carried out on all of the PL spectra of the samples with three different Cl concentrations as well as the undoped one. The extracted intensities of the Cl-donor-bound exciton as a function of laser power are then fitted to the \( I \sim L^k \) law, where \( I \) is the PL intensity...
and $L$ is excitation power, as plotted in Figure 3-9. Obtained from the fitting, the $k$ values for the three Cl concentrations from low to high are, respectively: $1.4 \pm 0.3$, $1.4 \pm 0.3$ and $1.5 \pm 0.2$. The intensity dependence $k$ of undoped sample is $2.0 \pm 0.3$ from the fitting.

![Figure 3-10](image)

**Figure 3-10** Log($I$) vs. log($L$) of the undoped and Cl-implanted 2nd quality NM crystal with three concentrations. $I$ is the intensity of the free-exciton line at 1.596 eV. $L$ is the laser power.

Intensities of the free-exciton transition as a function of laser power are also fitted to the $I \sim L^k$ law, as plotted in Figure 3-10. The $k$ values from fitting for the three Cl concentrations from low to high are, respectively: $1.0 \pm 0.3$, $1.0 \pm 0.3$ and $0.6 \pm 0.2$ (Table 3-3). The intensity dependence $k$ of the undoped sample is $1.6 \pm 0.2$ from the fitting.

**3.5.2 Free-Bound Transition**

In Figure 3-11, the four panels plot excitation-power-dependent PL in the free-to-bound region of the standard annealed NM CdTe crystal with
no-intentional doping and the three Cl concentrations in the crystal. For convenience of comparison, the spectra of lower powers are multiplied by the factors indicated except for the highest one 50 W/cm$^2$.

Figure 3-11  Excitation-power-dependent PL in the free-to-bound region of: a) undoped standard annealed 2$^{nd}$ quality NM crystal; b) CdTe:Cl 3x10$^{16}$ (cm$^{-3}$); c) CdTe:Cl 1x10$^{17}$ (cm$^{-3}$); d) CdTe:Cl 1x10$^{18}$ (cm$^{-3}$). PLs were excited by 488nm laser. Samples were cooled to around 40K.

The 1.549 eV transition line observed in the undoped 1$^{st}$ quality NM crystal (Figure 3-3a), which is a free-to-bound transition arising from an unknown residual impurity in the crystal, appears also in both of the undoped 2$^{nd}$ quality crystal and the Cl-implanted ones.
Figure 3-12  Log(\(I\)) vs. log(\(L\)) of the undoped and Cl-implanted 2\textsuperscript{nd} quality NM crystal with three concentrations. \(I\) is the integrated intensity of the Cl related free-to-bound transition and phonon replica. \(L\) is the laser power.

In these 2\textsuperscript{nd} quality crystals, the Cl-related free-to-bound transitions peak at 1.558 eV for the three Cl concentrations and the undoped crystal, instead of 1.553 eV in the 1st quality crystal. This transition overlaps strongly with the 1.549 eV line. Fortunately, these two transitions share approximately the same excitation power dependence and we can integrate them together for the intensities at different excitation powers. The spectral range between 1.52 to 1.57 eV is integrated, including the 1.5388 eV peak and its shoulder at \(\sim\)1.529 eV which are, respectively, the phonon replicas of the 1.558 and 1.549 eV transitions.

Intensities of the Cl-related free-to-bound transition as a function of laser power are then fitted to the \(I \sim L^k\) law. As plotted in Figure 3-12, the \(k\) values from fitting for the three Cl concentrations from low to high are, respectively, 0.8 ±
0.3, 0.8 ± 0.3 and 1.1 ± 0.3 (Table 3-3). The intensity dependence, \( k \), of the undoped sample is 1.2 ± 0.2 from the fitting.

### 3.5.3 Summary

The power dependent \( k \) values of the Cl-related valence-to-donor and donor-bound-exciton transitions as well as the free-exciton transition are summarized in Table 3-3. Values of \( K_{D^0,X} = k_{FE}/2 \) for the four different Cl concentrations (implanted and undoped) are computed too. According to Schmidt and Lischka’s prediction for the case that the concentration of neutral donors \( N_{D^0} \) and acceptors \( N_{A^0} \) depend on excitation power, \( L \), a relationship among \( k_{hD^0}, k_{FE} \) and \( k_{D^0,X} \) exists as described in Equation (2-19) in Chapter 2.

**Table 3-3** Summary of \( k \) values of Cl related transitions and free-exciton.

<table>
<thead>
<tr>
<th>sample</th>
<th>( k_{FE} )</th>
<th>( k_{D^0,X} )</th>
<th>( k_{D^0,X} - k_{FE}/2 )</th>
<th>( k_{hD^0} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>undoped</td>
<td>1.6 ± 0.2</td>
<td>2.0 ± 0.3</td>
<td>1.2 ± 0.4</td>
<td>1.2 ± 0.2</td>
</tr>
<tr>
<td>3E+16</td>
<td>1.0 ± 0.3</td>
<td>1.4 ± 0.3</td>
<td>0.8 ± 0.5</td>
<td>0.8 ± 0.3</td>
</tr>
<tr>
<td>1E+17</td>
<td>1.0 ± 0.3</td>
<td>1.4 ± 0.3</td>
<td>0.9 ± 0.5</td>
<td>0.8 ± 0.3</td>
</tr>
<tr>
<td>1E+18</td>
<td>0.6 ± 0.2</td>
<td>1.5 ± 0.2</td>
<td>1.1 ± 0.4</td>
<td>1.1 ± 0.3</td>
</tr>
</tbody>
</table>

As summarized in Table 3-3, the values of \( k_{hD^0}, k_{FE} \) and \( k_{D^0,X} \) for all the four Cl concentrations agree with Equation (2-19). This confirms that the free-to-bound transition at 1.558 eV and the donor-bound-exciton transition at 1.5905 eV share the same origin of impurity, which is most likely a Cl donor substituting on a Te site.
3.6 Temperature-Dependent PL

A temperature-dependent PL intensity study was carried out on the same chlorine-implanted crystals. PL spectra were collected in the temperature range from \( T = 8.6 \) to 100 K. Samples were cooled down by the liquid He refrigerator to 8.6 K and then gradually heated up with temperature steps of 10 degrees. The temperature was measured and controlled by a Lake Shore temperature controller DRC-91CA.

![Graph](image)

**Figure 3-13** Intensities of valence-to-Cl-donor transition at 1.560 ~ 1.556 eV, and theoretical calculation of one activation energy model: \( I/I_0 = C \exp(E_D/kT) \). The PLs were excited by 488nm laser with power density 15W/cm².

As we discussed in Chapter 2, the slope of the high temperature end of the Arrhenius plot provides the activation energy of the impurity. The temperature dependencies of the intensities \( I \) of the valence-to-donor (Cl donor) transition line at 1.560 ~ 1.556 eV, are fitted by a one-activation energy model.
For the case of $E_D \gg kT$, which in Section 3.3 an estimation has given $E_D = 53.0$ meV and the temperature $T < 100K$ ($kT < 8.6$ meV), $I/I_o = C \cdot \exp(E_D/kT)$ is a sufficiently good approximation. As represented in Figure 3-13, a 53.0 meV activation energy of the valence-to-donor transition is computed with the single-activation-energy model to fit the high temperature side of the curves. Two computed theoretical curves with a little variation of $I_o$ are compared with $I/I_o$ values from PL data of all the three Cl concentrations. Within the fitting error, the activation energy of 53.0 meV for the Cl donor in the CdTe crystal agrees well with the temperature-dependent PL.

3.7 Summary

The most apparent feature of PL on the Cl-doped CdTe is the substantial increase of the spectral intensities in the overall spectral region including the excitonic band, free-to-bound band and DAP in the deep-defect band. After implantation, a Cl-donor-related, free-to-bound emission line is also observed at 1.553 eV. The activation energy of the Cl donor in CdTe is identified to be 53.0 meV based on the peak position and temperature-dependent intensities of this free-to-bound line. The other interesting feature of Cl-implanted CdTe is that the bound-exciton emission lines shift to lower energy, and the DAP transition in the deep defect band enhances, with the increase of Cl dopants. These suggest the formation of Cl A-center acceptors in CdTe. An excitation-power-dependent PL study was performed on the undoped and Cl implanted CdTe crystals. The emission intensities of the 1.553 eV free-to-bound, the ~1.59 eV bound exciton and the 1.596 eV free exciton emission lines obey a power-law function of the
laser power. The exponents of these three emissions in the power-dependent function establish a relationship which demonstrates the Cl donor as the origin of both the free-to-bound and bound-exciton emission.
Chapter 4 Photoluminescence Identification of Phosphorus in CdTe Single Crystals

4.1 Introduction

Phosphorus, as a group V element, is an expected $p$-type dopant in CdTe material. Phosphorus doping into a CdTe thin film forming a low resistive and stable ohmic contact has been investigated by Ghosh et al.\textsuperscript{68} Using an autocatalytic reduction process, they deposited Ni-P composite material on the $p$-CdTe surface. The optimum P diffused CdTe $p^+$ layer achieved a contact resistivity down to 0.1~0.08 ($\Omega \cdot \text{cm}^2$), compared to the values of Cu-Au and Hg-doped graphite pasted contacts on CdTe film which are between 0.55 and 0.45 ($\Omega \cdot \text{cm}^2$). The latter two are the common contact formation methods in present CdTe thin film PV technology. Thermally evaporated CdS/CdTe solar cells deposited with the same Ni-P alloy are found to have higher $J_{sc}$ but lower $V_{oc}$ than regular cells with copper acceptor dopant.\textsuperscript{69}

It has also been observed by Bube et al\textsuperscript{70} that the hole concentration in P-doped CdTe films can reach $2 \times 10^{17}$ (cm$^{-3}$) with about 1.5\% of the incoming P incorporated as electrically active in the film. This is a much better $p$-type doping of CdTe compared to the average carrier concentration of $10^{14}$ (cm$^{-3}$)\textsuperscript{71} achieved with copper in a regular CdTe cell. An Ion-assisted doping (IAD) technique was used in Richard Bube’s work to control the phosphorus incorporation and $p$-type
doping of CdTe epitaxial films. This ion-assisted doping is similar to the
ion-implantation in my study, except that the ion energy is in a level of 100 eV for
IAD but 100 keV for ion-implantation. Also IAD injects ions during CdTe growth
while we implant ions into an already-made CdTe crystal.

Bube et al also found that phosphorus is completely electrically active up
to concentrations of $2 \times 10^{17} \text{cm}^{-3}$. At higher P concentrations, the carrier density
remained constant indicating decreased P fractional electrical activity. In our PL
study of a phosphorus ion-implanted CdTe crystal, as discussed below, P
concentrations are lower than $2 \times 10^{17} \text{cm}^{-3}$, indicating that 100% electrical activity
of the phosphorus can be assumed in all of the P implanted samples. Details of
the PL study are given below.

4.2 Sample preparation

As shown in Figure 4-1, three P ion kinetic energies were chosen for the
ion implantation into second quality NM CdTe wafers. The three P ion energies
are 350, 160 and 70 keV. To achieve a final uniform P profile below the wafer
surface, we selected 81.30, 17.89 and 0.81% of the total ion amount for the three
energies (Table 4-1), respectively, as indicated by Monte Carlo simulations in
SRIM. The ion concentration profile generated by SRIM has been plotted in
Figure 4-1. The projected range $R_p$ and the range straggling $\Delta R_p$ from the
simulation are, respectively, 0.284 and 0.159 \text{\mu m} (Table 4-1). The average
amount of vacancies generated by ion bombardment is 1792 (vacancies/ion).

The P species implanted into the CdTe crystal are then assumed to be
uniformly distributed from the surface to a depth of $R_p + \Delta R_p$. The 2$^\text{nd}$ quality NM
Figure 4-1 Simulated P atom distribution profile in CdTe after (solid line) 350, 160 and 70 keV implantation into the same target with $5\times10^5$, $1.1\times10^5$ and $5\times10^3$ P ions, respectively, and (dashed line) same amount of P ions for each energy but individual implanted.

Table 4-1 Summary of the Monte Carlo simulation of P implantation into CdTe crystals.

<table>
<thead>
<tr>
<th>Energy (keV)</th>
<th>$R_p$ (µm)</th>
<th>$\Delta R_p$ (µm)</th>
<th>Vacancies/ion</th>
<th>Fraction of Dose (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>0.0762</td>
<td>0.0411</td>
<td>629</td>
<td>0.81</td>
</tr>
<tr>
<td>160</td>
<td>0.1611</td>
<td>0.0785</td>
<td>1211</td>
<td>17.89</td>
</tr>
<tr>
<td>350</td>
<td>0.3355</td>
<td>0.1426</td>
<td>2091</td>
<td>81.30</td>
</tr>
<tr>
<td>70+160+350</td>
<td>0.2835</td>
<td>0.1590</td>
<td>1792</td>
<td>100</td>
</tr>
</tbody>
</table>

crystal was implanted with three different P concentrations: $1\times10^{15}$, $1\times10^{16}$, $1\times10^{17}$ (cm$^{-3}$) with the triple energy protocol described above. *Red phosphorus* powder was vaporized in the high vacuum chamber of the accelerator as the ion
source for implantation. CdTe wafers were also cut from same piece. Standard annealing, at 400 °C for 30 minutes in N₂ with the proximity cap of polycrystalline CdTe film, was carried out on the implanted wafer before PL acquisition, as described in Chapter 2 (Section 2.1).

After the implantation, all of the three P implanted wafers were etched in 0.05% Br methanol solution for 5 seconds to remove possible surface defects introduced by the manufacturer’s surface polish. This process has been measured to remove only 45Å CdTe on the surface.

4.3 Excitation Power Dependence

Power-dependent PL of P-implanted CdTe was carried out with excitation with the 488nm line of the Ar⁺ ion laser. Phosphorus concentration-dependent features have been identified as represented in Figure 4-2.

A free-to-bound emission at 1.556 eV corresponding to transitions of holes in the valence band to intrinsic Cl donors in the 2nd quality NM CdTe wafer, as has been discussed in Chapter 3, is observed in the spectra, as shown in Figure 4-2a. The intensities of this emission line do not depend on phosphorus concentration.

A transition at ~1.536 eV also appears in the P-implanted CdTe crystal (Figure 4-2a). It is easily confused with the phonon replica of the 1.556 eV Cl-related free-to-bound emission, which may also appear at 1.536 eV. However, the intensities of this emission line and its phonon replica at ~ 1.515 eV are observed to increase with phosphorus concentration in the samples, as shown in Figure 4-2a. We have identified the asymmetric shape of this 1.536 eV line and
fitted it with the *free-to-bound* transition model described in Chapter 2. This *free-to-bound* transition most likely corresponds to electrons in the conduction band recombining with holes on a neutral acceptor state \((eA^0)\) of phosphorus on the tellurium site \((P_{Te}^\circ)\).

![Figure 4-2](image)

**Figure 4-2**  a) PL of P-implanted 2\(^{nd}\) quality NM CdTe crystal with P concentration of \(1 \times 10^{15}\), \(1 \times 10^{16}\), \(1 \times 10^{17}\) (cm\(^{-3}\)), and b) spectra in the excitonic band range. PLs were excited with a 488nm laser beam focused to a power density of 11.7W/cm\(^2\). Samples were cooled down to approximately 40 K.
Eagles’s free-to-bound transition model\textsuperscript{45} was employed to fit the electron-to-P- acceptor transition lines as shown in Figure 4-3. The best fitting gives an electron temperature $T_e = 48 \ (\pm 1) \ K$ with the activation energy of $E_I = 70.6 \ \text{meV}$. The computation with peak energy ($E_{\text{peak}} = 1.5355 \pm 0.0002 \ \text{eV}$) and bandgap ($E_g = 1.604 \ \text{eV}$) also gives:

$$E_I = E_g - E_{\text{peak}} + \frac{K T_e}{2} = 70.6 \ (\pm 0.2) \ \text{meV}.$$ 

In the excitonic region, an acceptor-bound exciton recombination line peak at $1.588\sim1.589 \ \text{eV}$ (see Figure 4-2b) is observed. The shoulder at approximately $1.592 \ \text{eV}$ can be understood as the Cl-donor-bound exciton recombination.

Figure 4-3  Fitting conduction band to P acceptor ($eA^0$ at 1.5355 eV) and valence band to intrinsic Cl donor ($hD^0$ at 1.556 eV) transitions with Eagles’s model of free-to-bound transition line shape. Solid line: experimental PL spectrum of CdTe: P $1 \times 10^{17}$ (cm$^{-3}$) excited by $11.7 \text{W/cm}^2 488\text{nm}$. Broken line: model.
Figure 4-4  Excitation power dependence of the eA\(^0\) line at 1.5355 eV for three P concentrations. Lines are fitted to the \(I \sim L^k\) law, where \(I\) is the transition line intensity and \(L\) is excitation power.

The excitation power dependent PL spectra were excited with the 488 nm laser focused to power densities of: 0.5, 1.5, 5.6, 11.7 and 40.7 W/cm\(^2\). As one can tell in both Figure 4-2 and Figure 4-4, the intensity of the eA\(^0\) line at 1.5355 eV strongly depends on P concentration, which is the first evidence that the origin of this transition is the phosphorus impurity. The intensity of this line also increases with excitation power. The dependence of the eA\(^0\) line intensities are plotted in Figure 4-4. The plot of \(\log(I)\) vs. \(\log(L)\) clearly represents a straight line which is consistent with the \(I \sim L^k\) law.

The laser excitation power dependence, \(k\), of the 1.5355eV free-to-bound PL intensity is summarized in Table 4-2 and decreases with P concentration.
The exponent of the power dependence decreases by about 20% as the P concentration increases by a factor of 100.

Table 4-2  Excitation Power dependence $k$ of free-to-P-donor lines from P-implanted CdTe crystals

<table>
<thead>
<tr>
<th>P concentration (cm$^{-3}$)</th>
<th>$k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1 \times 10^{15}$</td>
<td>0.91 ± 0.03</td>
</tr>
<tr>
<td>$1 \times 10^{16}$</td>
<td>0.78 ± 0.02</td>
</tr>
<tr>
<td>$1 \times 10^{17}$</td>
<td>0.700 ± 0.008</td>
</tr>
</tbody>
</table>

4.4 Temperature Dependence

A temperature-dependent PL intensity study was carried out on the same phosphorus-implanted wafers. PL spectra were collected in the temperature range from $T = 8.6$ to 120 K. Samples were cooled down by the liquid He refrigerator to 8.6 K and then gradually heated up with temperature steps of 3, 5 or 10 degrees depending on how rapidly the PL features varied with temperature. Spectra were excited by the 488 nm laser with a power density of 560 (mW/cm$^2$) (5.6 suns).

Irrespective of the specific quenching mechanism, the temperature dependence of the intensity $I(T)$ of PL bands in CdTe is most often described by the expression:

$$I(T) = \frac{I(0)}{1 + C \cdot \exp(-E_A/kT)}$$

as given in Chapter 2. For the case of $E_A >> kT$, which in our case is expected to be $E_A \sim 70$ meV and the temperature $T < 100$K ($kT < 8.6$ meV), the PL intensity
can be approximated well with $I(T) \sim \exp(E_A / kT)$. The slope of the high temperature end of the Arrhenius plot will provide the activation energy of the impurity. For the convenience of comparing the absolute line intensities of different phosphorus concentrations, $\log[I(T)]$ is used for the ordinate axis in the
Arrhenius plot, instead of $\log\left[I(T)/I(0)\right]$ as usual. As represented in Figure 4-5a, intensities of the conduction-band-to-P-acceptor transition line at ~1.536 eV of the samples with three different P concentrations are fitted with the single-activation-energy model.

Fitting of the high temperature side to an $\exp(E_A/kT)$ curve in the Arrhenius plot indicates that the activation energies of the electron-to-P-acceptor line in the three P-implanted CdTe crystals apparently increase with phosphorus concentration, as summarized in Table 4-3. Fairly close activation energies have been obtained for the two higher P concentration samples ($1 \times 10^{16}$ and $1 \times 10^{17}$ (cm$^{-3}$)). The energies are 67.8 and 72.0 meV, respectively. However the sample with the lowest P concentration $1 \times 10^{15}$ (cm$^{-3}$) yields $E_A = 58.2$ meV, which disagrees with the other two. We do not fully understand this discrepancy but another approach to understanding this phenomenon will be discussed later.

<table>
<thead>
<tr>
<th>P concentration (cm$^{-3}$)</th>
<th>Activation Energy (meV)</th>
<th>Peak Position (eV) at T =8.6 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1 \times 10^{17}$</td>
<td>$72.0 \pm 0.8$</td>
<td>$1.5391 \pm 0.0002$</td>
</tr>
<tr>
<td>$1 \times 10^{16}$</td>
<td>$67.8 \pm 1.6$</td>
<td>$1.5391 \pm 0.0002$</td>
</tr>
<tr>
<td>$1 \times 10^{15}$</td>
<td>$58.2 \pm 1.2$</td>
<td>$1.5385 \pm 0.0002$</td>
</tr>
</tbody>
</table>

In 1983, E. Molva et al identified the ionization energy of the ground and first excited state of the P acceptors in CdTe at 68.2 and 17.3 meV.$^{72}$ They calculated the ionization energy of the phosphorus acceptor based on
observations of electron-to-acceptor $eA^0$ peak energy. In our study, fitting to the high temperature side of the Arrhenius plot confirms the shallow P acceptor level in CdTe with a ground energy level approximately 70.6 meV above the valence band ($E_v + 70.6$ meV) and depending upon phosphorus concentration.

Meanwhile, it is apparent that the intensity of this phosphorus-related, free-to-bound transition line depends on the P concentration when the temperature is higher than 30 K. However, when the temperature is lower than 30 K, the variation of intensities is complicated and does not simply depend on P concentration (Figure 4-5b). Yet one interesting feature can be synthesized as below.

The interesting result concerning the variation of the emission intensity is that for the two higher P concentrated samples - $1 \times 10^{17}$ and $1 \times 10^{16}$ (cm$^{-3}$), the intensity of this 1.536 eV electron-to-acceptor emission line increases initially and then decreases with increasing temperature (Figure 4-5b). The same phenomenon was observed by Bryant et al\textsuperscript{73} in electron-to-acceptor transitions, where the acceptor in their case was a cadmium vacancy $V_{Cd}$. The interpretation provided by Bryant et al can be understood as involving two thermal dissociation processes. Besides the ionization of the neutral acceptor, the dissociation of the exciton-neutral acceptor state is also involved. When the dissociation of neutral acceptor bound excitons occurs, excitons are released resulting in more neutral acceptors in the ground state for the 1.536 eV free-to-bound transition.

With increasing temperature, these two dissociation processes compete with each other. Apparently the thermal ionization results in fewer neutral
Figure 4-6  Intensities of neutral-acceptor-bound exciton (AX°) at ~1.589 eV decrease with temperature and disappear when T > 30 K.

acceptors available for the free-to-bound transition, while the dissociation of the bound-exciton generates more. When the temperature is as low as 9 K, most of the excess holes are frozen and trapped in acceptor states forming neutral acceptors. The photo-generated excitons could also be trapped by the neutral acceptors and screen them from free carriers outside the orbital of excitons. As the temperature increases but not high enough to ionize the neutral acceptors, the
neutral-acceptor-bound excitons are released due to the low activation energy and leave more un-screened neutral acceptors available for the conduction-to-acceptor transition. If the temperature continues to increase, acceptor ionization occurs, during which holes are thermally excited to the valence band and leave behind negatively charged acceptors \((A^-)\) which are not available for recombination with a free electron in the conduction band (refer to Figure 2-9).

If the dissociation of the bound excitons occurs in our phosphorus-implanted sample, the intensity of the 1.536 eV emission should increase initially with increasing temperature due to the dissociation of bound excitons and then decrease as in the normal case because of the thermal ionization of neutral acceptors, which has been observed (Figure 4-5b). Meanwhile the apparent intensity decrease of the neutral-acceptor-bound exciton \((AX^0)\) emission should also occur. This is observed as plotted in Figure 4-6. The \(AX^0\) emissions disappear beyond 30 K, which is consistent with the maximum intensity of the 1.536 eV eA\(^\circ\) emission at 27 K (Figure 4-5b). Thus, the activation energy of the neutral acceptor bound exciton was estimated to be 2.6 meV.

As to the temperature dependence of the transition line \((1.53 \sim 1.54 \text{ eV})\) intensity of the \(1\times10^{15}\) \((\text{cm}^{-3})\) sample, another understanding can be approached by a better fitting function with the two-activation-energy model. With two different activation energies \(E_{T1}\) and \(E_{T2}\), the intensity \(I(T)\) alters with temperature as the function:

\[
I(T) = \frac{I_0}{1 + C_1 e^{\frac{E_{T1}}{kT}} + C_2 e^{\frac{E_{T2}}{kT}}}
\]

\[\text{(4-2)}\]
The best fitting of this two-activation-energy model to the $1 \times 10^{15} \text{cm}^{-3}$ spectrum, as shown in Figure 4-7, gives $E_{T1} = 53.4 \text{ meV}$ and $E_{T2} = 9.5 \text{ meV}$.

![Graph showing temperature dependence of eA^0 line intensity at 1.53 ~ 1.54 eV of 1x10^{15} \text{cm}^{-3} \text{ P implanted CdTe fitted by the two-activation-energy model. (▲) experimental data, (line) fitting. \ E_{T1} = 53.4 \text{ meV and E}_{T2} = 9.5 \text{ meV are used in the model.}]

**Figure 4-7** Temperature dependence of eA^0 line intensity at 1.53 ~ 1.54 eV of 1x10^{15} \text{cm}^{-3} \text{ P implanted CdTe fitted by the two-activation-energy model. (▲) experimental data, (line) fitting. \ E_{T1} = 53.4 \text{ meV and E}_{T2} = 9.5 \text{ meV are used in the model.}]

As mentioned previously, the phonon replica of the Cl-related, free-to-bound emission at 1.556 eV should also be expected to appear at 1.536 eV. This emission could overwhelm the weak eA^0 emission of the phosphorus acceptor in this sample due to the low phosphorus dopant concentration. Therefore the activation energy of $E_{T1} = 53.4 \text{ meV}$ should be explained as the intrinsic Cl donors to the substrate material. This value is in good agreement with the ionization energy – state at 53.0 meV of the Cl donor in CdTe as identified in Chapter 3. And it is worthwhile pointing out that for this sample, the acceptor-bound exciton line of neutral P acceptor is not observed either (see Figure 4-2b).
Since the activation energy $E_{T2} = 9.5$ meV is within the range of the binding energy of exciton to impurity, this one can be understood as the binding energy between the bound exciton to the Cl donor.

4.5 Summary

A shallow acceptor state of phosphorus in CdTe is identified through a study of the free-to-bound emission in ion implanted crystals. The emission line peak energy is 1.5355 eV which is independent of phosphorus concentration. The ionization energy of neutral P acceptors is identified to be ~69 meV by the peak energy and confirmed by the temperature dependent PL study.

This shallow energy level of the phosphorus acceptor in CdTe suggests that phosphorus is a good candidate for $p$-type dopant, possibly to replace copper in CdTe based solar cells. The copper acceptor in a cadmium site is a deep acceptor in CdTe with an ionization energy of 146 meV. Even though copper has been proven to be useful for achieving heavy $p$-type doping of the CdTe at the contact, it is also a fast diffuser and can accumulate at the CdS/CdTe junction. Such accumulation is suspected of playing a role in cell deterioration under certain conditions.

Even though CdTe has a 1.5 eV bandgap at room temperature, the present best functional cells with a $p$-type dopant of copper operate with $V_{oc} \sim 0.85$ V. This indicates that there is still a wide space to improve the open circuit voltage without necessarily losing much $J_{sc}$. One method to approach higher $V_{oc}$ is to find another shallower acceptor dopant to substitute the copper (refer to the Appendix A). The shallow phosphorus acceptor could be a good candidate.
Chapter 5  Introduction to Extended X-ray Absorption Fine Structure

5.1  Introduction to Extended X-ray Absorption Fine Structure

Extended X-ray Absorption Fine Structure (EXAFS) is a powerful technique for understanding the lattice environment around selected elements. EXAFS is the fine structure in the x-ray absorption coefficient starting somewhat past an absorption edge and extending typically 1000 eV further, as shown in Figure 5-1.

After revealing the shell structure of atoms at the beginning of the last century, X-ray absorption spectroscopy was first used in the 1920s for structural investigations of materials. But only after the 1960s has its power for structure determination been appreciated. The first experimental detection of fine structure past absorption edges was by Fricke\textsuperscript{75} and Hertz\textsuperscript{76}. The observed fine structure near the absorption edges was first explained in general terms by a theory of Kossel\textsuperscript{77} and for many years was referred to as “Kossel structure”, which is now called XANES (x-ray absorption near edge structure) or NEXAFS (near edge x-ray absorption fine structure). In contrast, the structure extending for hundreds of electron volts past the edge was called “Kronig structure” after the scientist\textsuperscript{78} who germinated its theoretical explanation. The latter is what is now called extended X-ray absorption fine structure (EXAFS)\textsuperscript{79,89}

In spite of some applications made of EXAFS as an experimental tool,
Figure 5-1  a) Global view of x-ray absorption spectrum and b) EXAFS of a copper foil, which is in the range of around 1 keV beyond the absorption edge.

the lack of detailed agreement between any theory and the experiments left understanding of the structure of matter in a confusing situation, until Sayers et al.\textsuperscript{80} made a historical improvement on the theoretical expression\textsuperscript{81} of the EXAFS that has since become the accepted modern form. They pointed out that a Fourier transform of the EXAFS with respect to the photoelectron wave number should peak at distances corresponding to nearest-neighbor coordination shells of
The introduction of the Fourier transform changed EXAFS from a confusing scientific curiosity to a quantitative tool for structure determination. It was now possible to use EXAFS to extract structural information directly and to determine experimentally all the required atomic parameters.

In principle, x-ray absorption fine structure spectroscopy is based upon Beer’s law, the absorption is given by

\[ \mu x = \ln \left( \frac{I_0}{I_t} \right) \]  

(5-1)

where is \( \mu \) is the linear absorption coefficient and \( x \) is the sample thickness. The absorption coefficient as a function of incident x-ray photon energy - \( \mu(E) \), is the basic physical data measured in EXAFS.

To demonstrate EXAFS, an x-ray absorbance spectrum covering both soft (long-wavelength or low energy) x-rays and hard (short-wavelength or high energy) x-rays range is shown in Figure 5-1a. At an absorption edge of any element contained in the material, the absorbance increases suddenly and photoelectrons are excited. With a fine- step energy scan, a periodic oscillation structure with a certain frequency, or usually in most cases a combination of several different frequencies, can be observed beyond the absorption edge. This oscillation structure is the key to the EXAFS technique, which contains the information of the local structure surrounding the designated element.

X-ray absorption in the photon energy range up to 40 keV, the range of most importance for EXAFS, is dominated by photoelectron absorption where the photon is completely absorbed, transferring its energy to excite a photoelectron and leaving behind a core hole in the atom. Assuming that all the absorbed
photon’s energy goes into exciting a single core electron, the kinetic energy of the generated photoelectron is given by $E_k = E - E_o$ (Figure 5-2a), where $E = h\nu$ is energy of the absorbed x-ray photon and $E_o$ is the ionization energy of the electron shell. When the photoelectron has about 15 eV or greater kinetic energy, this energy is large compared with its interaction energy with the surrounding atoms ($\sim 3$ eV). In this case the interaction with the surrounding medium can be treated as a perturbation about an isolated atom. The final state of the photoelectron is modified to first order by a single scattering from each surrounding atom.

![Figure 5-2](image)

**Figure 5-2**  a) Generation of photoelectron and consequently X-ray Fluorescence and Auger electrons; b) propagation of scattered and outgoing electron matter waves.

Quantum-mechanically, the electron must be treated as a matter wave (Figure 5-2b) with wavelength given by the de Broglie relation $\lambda = h/p = h/(2m_e E_k)^{1/2}$. The propagation of the electron in the material is the propagation of a matter wave which can be scattered by neighbor atoms. For an isolated atom the photoelectron can be represented as a spherical outgoing wave of wave number $k$.
As indicated by the solid lines in Figure 5-2b, the amplitude of the outgoing wave is proportional to \( \exp(ik\vec{R})/R \). The neighboring atoms at position \( \vec{R}_i \) can elastically scatter the outgoing waves as shown by the dashed lines. Constructive and destructive interference between the scattered and outgoing electron waves determine how the final state of the photoelectron is modified by the surrounding atoms at the center of the absorbing atom. This interference leads to EXAFS, because a matrix element between the final and initial states of the photoelectron determines the absorption of the x-rays.

In EXAFS, the initial state is the electron in the atomic core and the final state is the electron excited to the escaping photoelectron. The final state of the photoelectron is the superposition of the outgoing and scattered waves. When the local structure of the core atom is stable, the relative phase differences between scattered and outgoing waves are functions of the wavelength, \( \lambda \), which is actually tunable by the incident x-ray photon energy \( E \), that is

\[
\lambda = \frac{h}{\sqrt{2m_eE_k}} = \frac{h}{\sqrt{2m_e(E - E_o)}}
\]

(5-2)

The total amplitude of the electron wave function will then be modified by the phase difference, thus modifying the probability of absorption of the x-ray correspondingly. Thus the variation of the fine structure in EXAFS, as shown in Figure 5-1, is a direct consequence of the wave nature of the photoelectron.

It is actually not difficult to translate the qualitative picture as described above into an expression for EXAFS. The amplitude of the backscattered spherical wave \( \exp(ik|\vec{R} - \vec{R}_i|/|\vec{R} - \vec{R}_i|) \) is proportional to the product of the amplitude
of the outgoing wave at the position $\vec{R}_i$, and a backward scattering amplitude $T_i(2k)$ characteristic of the back scatter, that is

$$T_i(2k) \cdot \frac{\exp(i k \vec{R}_i)}{R_i} \cdot \frac{\exp(i k |\vec{R} - \vec{R}_i|)}{|\vec{R} - \vec{R}_i|}.$$  

(5-3)

When the scattered electron wave arrives back at the origin ($R = 0$), the backscattered spherical wave in equation (5-3) has an amplitude proportional to $T_i(2k) \cdot \exp(i 2k R_i) / R_i^2$, where the factor $2k R_i$ is the phase shift introduced by the wave traveling distance $2R_i$ from the origin and back from the backscatterer. Along the way, the electron moves out of and into the varying potential of the center atom and also senses the varying potential of the backscattering atom. These potentials add additional phase shifts that we can call $[\Phi_i - (\pi/2)]$. The complex expression for the backscattered wave becomes:

$$T_i(2k) \cdot \exp[i 2k R_i + \Phi_i(k) - \pi/2] / R_i^2.$$  

(5-4)

The backscattered wave at the origin modifies the absorption while interfering with the outgoing wave. This modification by definition is the EXAFS. Thus the real part of Equation (5-4) is proportional to EXAFS, which is denoted by $\chi_i(k)$,

$$\chi_i(k) \sim \frac{T_i(2k)}{R_i^2} \sin[2k R_i + \Phi_i(k)].$$  

(5-5)

In many materials, the surrounding atoms arrange themselves into coordination shells where the distances from the central atom to the atoms in a shell are approximately equal and there is only one atomic species in each shell. In this case EXAFS can be interpreted as the synthetic output of scattering from different atomic shells, which are called scattering “paths.”
\[ \chi(k) = \sum_{\Gamma} \chi_{\Gamma}(k) \] (5-6),
where \( \Gamma \) is the atomic shell index. Of course single scattering paths and multiple scattering paths are all considered. For an unoriented sample with small or approximately Gaussian disorder, each path contribution is described by\(^{83} \) (note: the phase shift of \( \pi/2 \) in equation (5-4) is not included in this equation; thus the imaginary part is calculated, instead of real part, to obtain \( \sin[2kR_\Gamma + \Phi_{\Gamma}(k)] \))

\[ \chi_{\Gamma}(k) = \text{Im} \left( \frac{N_\Gamma S_o^2 F_\Gamma}{kR_\Gamma^2} e^{i(2kR_\Gamma + \Phi_{\Gamma})} e^{-2k^2 \sigma_\Gamma^2} e^{-2R_\Gamma/\lambda} \right) \]

\[ = \frac{N_\Gamma S_o^2 F_\Gamma}{kR_\Gamma^2} \sin(2kR_\Gamma + \Phi_{\Gamma}) e^{-2k^2 \sigma_\Gamma^2} e^{-2R_\Gamma/\lambda} \] (5-7)
where

\[ R_\Gamma = R_{o,\Gamma} + \Delta R_\Gamma \] (5-8)

\[ k = \sqrt{\frac{2m(E - E_o)}{\hbar^2}} \] (5-9)

More precisely,\(^{84} \)

\[ \chi_{\Gamma}(k) = \frac{N_\Gamma S_o^2 kF_\Gamma}{kR_\Gamma^2} \exp(-2R_\Gamma/\lambda) \sin(2kR_\Gamma + \Phi_{\Gamma,\text{eff}} + \Phi_c) \exp(-2k^2 \sigma_\Gamma^2) \] (5-10)
where

- \( E_o \): Overall absorption threshold shift
- \( k \): The wave number in units of Å\(^{-1}\) as defined as in (5-9)
- \( \Phi_c \): The total central atom phase shift
- \( F_\Gamma \): The effective magnitude of the backscattering amplitude for each path
- \( \Phi_{\Gamma,\text{eff}} \): The phase shift for each shell
- \( \kappa \): The total central atom loss factor, \( \kappa = \exp(-2\text{Im}(\delta_c)) \)
- \( R_\Gamma \): The distance to central atom for each shell – path length
\[ R_{\text{r}} \quad \text{The path length in the reference material} \]

\[ \Delta R_{\text{r}} \quad \text{The path length correction in the unknown material} \]

\[ N_{\text{r}} \quad \text{The mean number of atoms in each shell} \]

\[ \sigma_{\text{r}}^2 \quad \text{The mean square fluctuation in } R_{\text{r}} \text{ for each shell} \]

\[ \lambda \quad \text{The mean free path in Å, } \lambda = 1/|\text{Im}(p)| \]

5.2 EXAFS Instrumental and Data Analysis

Several techniques for measuring EXAFS have been developed, such as transmission, fluorescence and Auger detections as described in Figure 5-3, each with its advantages and disadvantages.

5.2.1 Experiment Design

5.2.1.1 Transmission Detection

The most widely used method is to measure the absorption of a sample by monitoring the incident, \( I_0 \), and transmitted, \( I_t \), flux intensity, as shown in Figure 5-3. The absorption \( \mu \) is then given by equation (5-1). This method is simple to apply and makes use of all photons incident on the sample. Using a monochromator to select a small wavelength range \( \Delta \lambda \) of the incident beam and monitoring \( I_0 \) and \( I_t \) with suitable detectors, a full EXAFS spectrum can be acquired by sequentially stepping the monochromator through the required energy range.

It is often possible to apply the transmission detection method in conjunction with other detection methods, such as a reference monitor on a Cu foil for photon energy calibration taking advantage of the scattered x-ray photons
Figure 5-3  Principle and mechanism of three EXAFS detection techniques in transmission, fluorescence and Auger modes (from left to right).

Figure 5-4  Experimental set up at the MRCAT beamline Hutch B.  Both transmission mode and fluorescence mode are set up for EXAFS collection.

as shown in Figure 5-4.  With this setup, the transmitted intensity of the x-ray beam through a thin copper foil is detected simultaneously with EXAFS data collection by fluorescence detection, to monitor potential photon energy
aberration due to monochromator distortion during data collection, since the characteristic elemental copper absorption edge does not shift. The x-ray is scattered by a tilted thin Al foil on the incident beam facing the reference monitor.

Gas ionization detectors are commonly used as integrating detectors to measure beam flux rather than individual photons, especially for measuring the flux of the incident synchrotron beam and the transmitted beam when transmission detection is applied for EXAFS collection. A typical detector consists of a rectangular gas cell with thin polymer film entrance and exit windows. Inside the detector, an electric field of about 100 V/cm is applied across two parallel plates and the electrons are collected at the anode plate. Some of the x-rays in the beam interact with the chamber gas to produce fast photoelectrons, Auger electrons, and/or fluorescence photons. The energetic electrons produce additional electron-ion pairs by inelastic collisions, and the photons either escape or are photoelectrically absorbed. The electrons and ions are collected at the plates, and the current is measured with a low-noise current amplifier (with an adjustable gain: volts output/ amps input). The x-ray flux is then proportional to the output voltage.

The efficiency of the detector can be calculated from the active length of the chamber, the properties of the chamber gas, and the x-ray absorption cross section at the appropriate photon energy. Figure 5-5 shows, for different gases at atmospheric pressure, the efficiency of a 10-cm-long ion chamber as a function of energy. Once the efficiency is known, the photon flux can be estimated from chamber current and the average energy $E_{\text{ei}}$ (Table 5-1) required to produce an
electron-ion pair:

\[
\text{Photon Flux (photons/sec)} \times h \nu \text{ (eV/photon)} \times 1.6 \times 10^{-19} \text{ C/electron} \times \frac{1 \text{ (electron)}}{E_{ei} \text{(eV)}} \times \text{Gain Factor (V/A)} = \text{Output Voltage (V)}
\]

**Figure 5-5** Efficiency of a 10-cm-long gas ionization chamber vs. photon energy, for different gases at atmospheric pressure.\(^8^5\)

**Table 5-1** Average energy required to produce an electron-ion pair in gases\(^8^5\) in the photon energy range of 0.2–50 keV (current mode).

<table>
<thead>
<tr>
<th>Element</th>
<th>Energy (eV) - (E_{ei})</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>41</td>
</tr>
<tr>
<td>(N_2)</td>
<td>36</td>
</tr>
<tr>
<td>Air</td>
<td>34.4</td>
</tr>
<tr>
<td>Ne</td>
<td>36.3</td>
</tr>
<tr>
<td>Ar</td>
<td>26</td>
</tr>
<tr>
<td>Kr</td>
<td>24</td>
</tr>
<tr>
<td>Xe</td>
<td>22</td>
</tr>
</tbody>
</table>
5.2.1.2 Fluorescence and Auger Electron Detection

In many cases transmission detection loses its advantage when the EXAFS signal is only a small fraction of the total absorption. Isolating the EXAFS from the background in transmission then requires the subtraction of two nearly equal signals. In these cases, it is desirable to measure the absorption by monitoring processes that are proportional to the absorption so that the enhanced signal of interest can be discriminated from the background.

![Graph showing Fluorescence yields for K and L shells for 5 ≤ Z ≤ 110.](image)

**Figure 5-6** Fluorescence yields for K and L shells for $5 \leq Z \leq 110$. The plotted curve for the L shell represents an average of L$_1$, L$_2$, and L$_3$ effective yields.\(^{86}\)

Two of these processes, x-ray fluorescence and emission of Auger electrons, as illustrated in Figure 5-3, are usually monitored under these circumstances. These two are competing processes. Their relative strengths depend on the atomic number of the absorber. In light elements Auger emission is more probable, while for heavy elements fluorescence becomes more likely.
For the same element, fluorescence is more likely for K-shell holes than for L-shell holes, as shown in Figure 5-6. These yields represent the ratio of the probability of a core hole in the K or L shells being filled by a radiative process, in competition with nonradiative processes. Auger processes are the only nonradiative processes competing with fluorescence for the K shell and L\textsubscript{3} subshell holes. However, no measurement through Auger processes is used in this study. Thus our discussion will focus on the fluorescence detection method which is the major measurement technique in this study.

The fluorescence radiation results from the filling of the core hole generated by the absorption of an x-ray photon. For example, the K shell is dominated by the production of K\textsubscript{α} radiation. Copper K\textsubscript{α} is the main process used in this study.

A 13-element high purity germanium semiconductor diode detector is employed to collect the x-ray fluorescence photons in this study. Semiconductor detectors are always fabricated in the structure of a p-n diode. The properties of the p-n junction are that it is highly conductive when a voltage (also called bias) is applied in the “forward” direction, but it is insulative (or conducts very little current) when biased in the “reverse” direction.

Reverse bias refers to a negative voltage being applied to the n side of the junction with respect to the p side. Under reverse bias, the natural potential difference across the junction is enhanced, as shown in Figure 5-7b. Under this circumstance, it is the minority carriers (holes on the n side and electrons on the p side) that are separated across the junction. Because their concentrations are
relatively low, the reverse current across the diode is quite small. Meanwhile, the concentrations of majority carriers (electrons on the $n$ side and holes on the $p$ side) decrease due to the potential bias applied on the two sides of the diode, and the corresponding depletion widths on either side are enlarged, as shown in Figure 5-7b. The principle of this phenomenon is readily available in many publications about semiconductor diodes.

![Figure 5-7](image.png)

**Figure 5-7** Electron energy bands across the $p$-$n$ junction of (A) non-biased diode and (B) reverse biased diode, and electric field $\varepsilon$ across the junction of (a) non-biased and (b) reverse biased diode. $V_c$ is the built-in potential of the $p$-$n$ junction. $V$ is the magnitude of reverse bias potential. $D_p$ and $D_n$ are, respectively, the depletion widths of $p$ side and $n$ side, which both increase under reversed bias.

Particularly, in application, one side of the semiconductor diode detector (such as the $p$ side) is usually doped at a much higher level than the other side ($n$
side), so that \( N_D \gg N_A \). Then the depletion width on the heavily doped side is small compared to the lightly doped side, that is \( D_p \gg D_n \). The depletion width of the lightly doped side is then approximately \(^{87}\)

\[
D = \sqrt{\frac{2eV}{eN}}
\]

where \( N \) represents the dopant concentration on the side with lower dopant level, \( e \) represents the dielectric constant, and \( V \) represents the reverse bias potential.

In practical operation, the semiconductor diode detector is usually completely depleted under reverse bias so that the depletion region extends all the way through the semiconductor wafer. This is for the purpose of generating an electric field everywhere in the absorber so that all of the radiatively generated electron-hole pairs can be separated and collected at the two poles of the diode. Even further, it is preferable to apply sufficient over-voltage (higher than that enough for complete-depletion) so that the electric field is high enough to impart saturated drift velocities to the charge carriers, minimizing the collection time and the detrimental effects due to carrier recombination and trapping.

Semiconductor diode detectors are generally among the fastest of all commonly used radiation detectors. Under normal conditions, the observed pulse rise time is of the order of 10 ns or less.

The dominant advantage of semiconductor detectors lies in the smallness of the ionization energy, usually noted as \( \varepsilon \). The values of \( \varepsilon \) at 77 K are 3.76 eV in silicon and 2.96 eV in germanium,\(^ {88} \) compared with about 30 eV required to create an ion pair in typical gas-filled detectors (see Table 5-1). Thus, for a given energy of the photon deposited in the detector, the number of charge
carriers is 10 times greater for the semiconductor detector. Since the detectors recognize the energy of the absorbed photon or high energy particle through the number of electron-hole pairs generated, the increased number of charge carriers in semiconductor detectors has beneficial effects on the attainable energy resolution. Particularly, the dominant characteristic of Ge detectors is their excellent energy resolution in the $\gamma$-ray spectroscopy energy range. The best performance of Ge detectors for x-rays is given by small planar detectors due to lower capacitance values (causing electronic noise) and carrier loss because of trapping (intrinsic impurities and defects).

Under reverse bias in the normal fashion applied to the detector junction, a small leakage current of the order of a fraction of a microampere is normally observed. A significant part of the leakage current is due to the thermal generation of electron-hole pairs within the depletion region, the probability of which is given by:

$$p(T) = CT^{3/2} \exp\left(-\frac{E_g}{2kT}\right),$$  \hspace{1cm} (5-12)

where, $T$ represents the absolute temperature, $E_g$ is the bandgap energy of the semiconductor, $C$ is a constant characteristic of the material. Because of the small bandgap (0.7 eV), room-temperature operation of Ge detectors is impossible due to the large thermally-induced leakage current. Instead, Ge detectors must be cooled to reduce the leakage current. The temperature is normally reduced to 77 K through the use of an insulated Dewar flask in which a reservoir of liquid nitrogen is kept in thermal contact with the detector.
5.2.2 Data Collection and Extraction

Before we go into more details, a concept issue needs to be addressed. X-ray absorption fine structure includes two independent parts: x-ray absorption near edge structure (XANES) and the extended x-ray absorption fine structure (EXAFS). The XANES is the absorption fine structure spectrum covering the range between the absorption edge of the element itself and the point usually considered to be 50 eV beyond the threshold. Practically, EXAFS is the range beyond the XANES region (see Figure 5-8). The XANES region is interesting because the amplitude of the periodic oscillatory structure in this range is always stronger than in the EXAFS region. Therefore the structure of XANES is useful for qualitative study as the fingerprint of unknown samples. Comparison of unknown and reference spectra in the XANES region is usually the first step of x-ray absorption fine structure data analysis.

It is worth pointing out that EXAFS also refers to the periodic oscillatory structure in the absorption spectrum above the edge due to the interference between back-scattered and out-going electron waves. (EXAFS in this meaning is usually noted as the \( \chi \) function as discussed in Section 5.2.2.3 and represented in Figure 5-10.) This oscillatory structure is the key to the EXAFS technique. The lattice environments are derivable from absorption spectra by Fourier transforming the EXAFS spectrum into a phase-uncorrected radial distribution function as pointed out by Sayers et al. in the history.\(^8^9\) More details follow.
5.2.2.1 Multiple Scans and Average Data

When EXAFS data are collected in the transmission mode, after attenuation by the sample material, a relatively low count rate of transmission flux may be detected compared to incident flux. When deexcitation processes – fluorescence and Auger electron emission are applied for EXAFS data collection, since usually these two are used for material with low concentrations of the element of interest, the low count rate of fluorescence intensity and Auger electron current is also an issue. To minimize the noise level, multiple scans are necessary. Meanwhile, if data are collected in fluorescence mode, multi-element-detectors are commonly used with multiple channels collecting the fluorescence signals simultaneously. All of these make averaging of multiple scans and/or scans from different detectors inevitable first step for EXAFS data processing. In this study, the average concentration of copper is around 0.3% in all the samples and data were always collected in fluorescence mode with a 13-element-Ge -detector. There are usually 10 or 11 good channels for data collection. An averaging process was necessary in the data analysis of this study.

To demonstrate the proper data analysis procedures, a copper foil absorption spectrum collected in transmission detection mode and the well known copper crystal structure will be used.

5.2.2.2 Pre-edge Background Removal

In EXAFS data, one is usually interested only in the region above the absorption edge. However, the region below the edge (Pre-edge) is affected by
lower energy absorption edges, Compton scattering, and other processes that are not of immediate interest. Other effects will be the different energy responses of the detectors, and also harmonic contamination in the beam or nonlinearities in the electronics. The quantity $\ln(S_0/S)$, where $S_0$ and $S$ are the signals from the detectors (before and after the sample, respectively), contains not only the absorption spectrum but also an energy-dependent term that represents the nonideal response of the apparatus. For example, the negative value in the pre-edge region of the copper foil in Figure 5-8 is obviously due to the larger

![Graph showing XANES and EXAFS regions]

**Figure 5-8** Average of 10 EXAFS scans on a copper foil. The dashed line is an estimated pre-edge background.

Fortunately the variation of detector efficiency between different detection instruments usually changes much slower than the EXAFS feature and it can be assumed to be a linear function. All of these effects unrelated to EXAFS are usually contained in not only the pre-edge but also the overall spectra region.
For instance, the declining tendency with increasing energy in the overall spectrum (Figure 5-8) is mostly due to the copper L edge (see Figure 5-1). Therefore a normalization process to remove the pre-edge feature is essential.

Subtracting out this pre-edge background will simplify later data normalization. The pre-edge removal generally involves a fitting to the data below the edge to some functional form and extrapolation of this function into the data region. Generally, a simple polynomial routine is most convenient where either a linear or quadratic polynomial function of photon energy can be used for absorption data and usually a linear polynomial is sufficient for fluorescence data.

5.2.2.3  Post-edge Background Subtraction

The main purpose of this process is isolating the fine-structure oscillations from absorption spectra. In general, the oscillatory part of the x-ray absorption coefficient is normalized by the smooth monotonically decreasing cross section of the edge of interest, $\mu_o(E)$, according to the equation that defines the EXAFS function:

$$\chi(E) = \frac{\mu(E) - \mu_o(E)}{\mu_o(E)}.$$  \hspace{1cm} (5-13)

Theoretically, $\mu_o(E)$ is the absorption assuming no electron scattering by neighbor atoms. However, $\mu_o(E)$ in general is neither measurable independently nor can it be calculated accurately, especially near an absorption edge.

In our data analysis, an edge-step normalization of the data is used. This means that the difference between $\mu(E)$ and $\mu_o(E)$ is divided by the value of
\( \mu_0 \) at the edge rather than by the functional form of \( \mu_0(E) \), as shown in Figure 5-9 respectively.

\[
\chi(E) = \frac{\mu(E) - \mu_0(E)}{\Delta \mu(E_0)}.
\]

(5-14)

**Figure 5-9**  Extraction of the Fine-Structure Oscillations in copper foil EXAFS data.

Since both the fine-structure oscillation amplitude \( \mu(E) - \mu_0(E) \) and edge-jump height \( \Delta \mu(E_0) \) are proportional to the quantity of the designated element in the material under x-ray exposure, this step actually eliminates sample thickness or concentration effects so that different samples will be directly comparable. Thus post-edge background removal intrinsically involves an energy-independent normalization.

To isolate the fine-structure oscillations, which are also named EXAFS, there are several commonly used methods all of which are dependent on the background being slowly varying compared with the EXAFS oscillations. These methods include the subtraction of:
1. a cubic least-squares-spline approximation to the data,
2. a simple polynomial background, followed by digital high-pass filtering,
3. a cubic smoothing-spline approximation to the data as the theoretical “smooth background” - $\mu_0(E)$.

The first technique is recommended for most applications. A cubic spline curve is constructed out of linked cubic polynomials; the function value and first derivative are matched at the knots where the polynomials meet. The number of knots is variable and depends on the particular data; typical values range from 2 to 6.

The other two methods are either limited in practice or desirable for special cases only. They are barely used in my studies. More details are available in reference\textsuperscript{89}.

In general, spline smoothing is more flexible. In my studies, the analyses are mainly performed in a computer code IFEFFIT\textsuperscript{90}, which has extended the spline fit as part of an iterative background removal scheme. The basic idea of this method is to make a spline fit with an initial guess for the smoothing parameter, subtract the data from the spline fit, Fourier transform the resulting $\chi$ data, and examine the low-frequency (mostly arising from background) components and the first-shell peak of the data transform to evaluate whether the background curve has frequency components high enough to modify the data. If true, the process is repeated with a higher value for the smoothing parameter.
Actually, a conversion from E to k space has been done before background subtraction so that the background fit does not preferentially follow the data at high energy (which oscillate slowly in energy space). After background subtraction, the experimental EXAFS function $\chi$ is obtained. $\chi(k)$ is preferred for the purpose of further procedure – Fourier transformation of $\chi$ function from k space to r space (Section 5.2.2.4).

**Figure 5-10**  
(a) $k^2$ weighted $\chi(k)$ function of a copper foil EXAFS spectrum.  
(b) $\chi(k)$ function of the copper foil EXAFS, without weighting.

The oscillation amplitude of the directly extracted EXAFS function $\chi(k)$ usually decays with k, as shown in Figure 5-10b. This is because the
neighboring atom scattering cross section for free electrons decreases with electron kinetic energy. To emphasize the \( \chi(k) \) function, the EXAFS function is always weighted by \( k^n \). The higher \( n \) is (usually 1, 2 or 3), the more emphasis on contributions from higher Z scatterers. For this study \( n=2 \) is large enough for suspected neighbors (Te, Cu, O, Cl and so on). A demonstration of the \( k \) weighted \( \chi(k) \) function of copper foil is shown in Figure 5-10a, and the corresponding unweighted \( \chi(k) \) in Figure 5-10b.

### 5.2.2.4 Forward and Inverse Fourier Transforms

At this point, the data consist of sums of damped sine waves corresponding to the different shells of atoms. As shown in Figure 5-10, one can easily tell that there are at least two different frequencies of oscillation in the \( \chi(k) \) function. A Fourier transform is a necessary process for spectral isolation in decoupling EXAFS parameters here.

It is known in mathematics that the Fourier transform of a periodic oscillation function, either \textit{sine} or \textit{cosine}, gives the delta function of the oscillation frequency, and the FT of a composite function of \textit{sine} and \textit{cosine} functions generates the delta functions of the corresponding frequencies. As long as \( k \) and \( r \) together determine the phase (\( \theta=2\pi kr \)) of the oscillation, the Fourier transform of the oscillation function of either \( k \) or \( r \) will generate the other one as the frequency. Also when the oscillation contains multiple frequencies, they can be isolated through the Fourier transform into multiple peaks of delta functions.
Therefore, in an EXAFS analysis, a complex Fourier transform of the data is then performed:

\[ F_x[\sin(2\pi r_0 k)](r) = \int_{-\infty}^{\infty} e^{-2\pi i k r} \left( \frac{e^{2\pi i r_0 k} - e^{-2\pi i r_0 k}}{2} \right) dk = \frac{1}{2} [i\delta(r + r_0) - \delta(r - r_0)] \]  

(5-15)

\[ F_x[\cos(2\pi r_0 k)](r) = \int_{-\infty}^{\infty} e^{-2\pi i k r} \left( \frac{e^{2\pi i r_0 k} + e^{-2\pi i r_0 k}}{2} \right) dk = \frac{1}{2} [i\delta(r - r_0) + \delta(r + r_0)] \]  

(5-16)

Therefore, the Fourier transforms of the EXAFS data are calculated for the copper foil.

A Fourier Transform of the \( \chi(k) \) function of copper foil EXAFS data is plotted in Figure 5-11. The first primary peak located at 2.24Å arises from the nearest-neighbor shell in the copper FCC crystal structure at the distance 2.55Å, which includes 12 copper atoms in this shell. If the center atom is the one on the center of one side face of the FCC unit cell (as denoted with darker color in Figure 5-11 b), the atoms in the 1st nearest-neighbor shell are those corner atoms of the square faces. The 2nd and 3rd peaks at 3.41Å and 4.14Å, respectively arise from the 2nd and 3rd neighbor shells at distances 3.61 Å and 4.42 Å. The 2nd
nearest-neighbor shell has 6 copper atoms which locate at the projective site on the opposite face and have the same distance as the lattice constant of 3.61 Å from the center atom. The 3rd shell includes 24 atoms locating at the corners of the opposite square face.

![Figure 5-11](image)

**Figure 5-11** (a) Fourier Transform of copper foil χ(k) function; (b) FCC structure of copper crystal, in which the nearest-neighbor shells are at the distance of 2.55, 3.61 and 4.42 Å.

**Table 5-2** Comparison of scattering peak positions and corresponding path lengths. The differences are due to the phase shift of photoelectron traveling in the Coulombic potential wells of original and scattering atoms.

<table>
<thead>
<tr>
<th>Shells</th>
<th>Peak positions (Å)</th>
<th>True path length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1&lt;sup&gt;st&lt;/sup&gt;</td>
<td>2.24</td>
<td>2.55</td>
</tr>
<tr>
<td>2&lt;sup&gt;nd&lt;/sup&gt;</td>
<td>3.41</td>
<td>3.61</td>
</tr>
<tr>
<td>3&lt;sup&gt;rd&lt;/sup&gt;</td>
<td>4.14</td>
<td>4.42</td>
</tr>
</tbody>
</table>

The difference between peak location in Fourier transformed χ(k) and the actual shell distance, or “path length” as it is usually named by EXAFS experts, is...
due to the phase shifts of photoelectrons, as $\Phi_{i,\text{eff}}$ and $\Phi_c$ defined in equation (5-4) and (5-10). Thus even though the Fourier transform is related to the path length distribution function, it is not a true radial distribution function. Among EXAFS workers, $\chi(r)$ is preferably called the phase-uncorrected radial distribution function. It is always found that the peak in $\chi(r)$ occurs at distances shorter than the physical path length of the corresponding neighbor shell (Table 5-2).

In the phase-uncorrected radial distribution function $\chi(r)$, features with very short path length such as below 1 Å are usually artificial error due to insufficient background subtraction which leak low frequency oscillations into $\chi(k)$. After the Fourier transform of $\chi(k)$, oscillation frequencies are separated and the insufficiently subtracted background part generates spurious small $r$ features in $\chi(r)$. Meanwhile large $r$ features in $\chi(r)$, empirically beyond 6 or 8 Å, depending on the materials which are studied, are usually weak and come from much higher frequency oscillations than real EXAFS features in the $\chi(k)$ function. These usually involve data noise and glitches in the original data. Thus the most valuable part in the $\chi(r)$ spectrum is located in the intermediate path length range from 2 to 6 Å.

The transformed data actually consist of a complex function, which has real and imaginary parts, or alternatively a modulus and phase. The modulus is the most frequently used quantity, but the real and imaginary parts are also useful. They exhibit significantly more structure than the modulus does, and they don’t suffer from nonlinear interference. The Fourier transform is a linear operation, that is, the Fourier transform of a sum of sine waves in $k$-space is also just the
sum of the Fourier transforms of the different contributions. Calculation of the modulus, however, is a nonlinear operation (the modulus of the sum is not the sum of the moduli). Therefore adjacent peaks can interfere with each other in the “transformed” function, rather than superimpose on each other. Often peaks which are not resolved from each other interfere strongly enough that there is a sharp dip in the modulus between the peaks, which may approach zero. Later on, we will see this appears in the forward Fourier transformed EXAFS function of Cu$_2$Te in Chapter 7. An $r$-window and inverse Fourier transform is then frequently used in extracting the scattering shell out of the interference so that certain peaks of the unknown shells are comparable to a standard. A window function in $r$-space is chosen that gives suitably isolated peaks in $r$-space and the peaks outside the $r$-space range of interest are set to zero and the data set is inverse-transformed to $k$-space:

$$\chi_{\alpha,\beta}(k) = \int e^{ikr} \tilde{\chi}_\alpha(r) W_\beta(r) \, dr$$  \hspace{1cm} (5-18)

where $W_\beta(r)$ is the $r$-window function, which depends on parameters denoted by the subscript $\alpha$. However, the reverse Fourier transform was not frequently performed in this study.

### 5.2.3 FEFF Theoretical Fitting

Once the phase and amplitude functions for the appropriate shells in the standards and unknown are determined, structural information can be obtained, such as coordination numbers and path lengths. To evaluate the total $\chi(k)$, IFEFFIT evaluates values for the various path parameters - $\Delta R$, $\sigma^2$, ($N\sigma S_0^2$), $E_0$ in the EXAFS equation (5-7)$^{92}$ for each path. The evaluation compares the $\chi_{data}(k)$
extracted from experimental data with standard paths $\chi_{th}(k)$ theoretically computed by an *ab initio* multiple scattering modeling code of FEFF. The FEFF theoretical computation is significant for obtaining the structure information in unknown samples. Thus this theoretical evaluation procedure is called “FEFF fitting”.

In the FEFF fitting, a fit by minimizing the function as below is performed in the program IFEFFIT:

$$
X^2 = \frac{N_{idp}}{N_{pts}} \sum_{l=1}^{N_{pts}} \left\{ \left[ \text{Re}(\tilde{\chi}_{true}(R_i)) - \tilde{\chi}_{th}(R_i) \right]^2 + \left[ \text{Im}(\tilde{\chi}_{true}(R_i)) - \tilde{\chi}_{th}(R_i) \right]^2 \right\}
$$

(5-19)

where

$N_{pts}$ is the number of points in the fitting range of the data. A $k$-grid of 0.05 Å$^{-1}$ is used in IFEFFIT. Thus the Fourier transformed data are written to a grid of about 0.003 Å. If the fitting is from 1 to 4 Å, $N_{pts} = 101$.

$N_{idp}$ is the number of independent points in the measurement. In IFEFFIT, EXAFS data are treated as a bandwidth-limited signal processing problem and the bandwidth is a function of the Fourier transform range multiplied by the fitting range. Specifically, $N_{idp} = \frac{2\Delta k\Delta R}{\pi} + 1$.

Typically, $N_{idp} \ll N_{pts}$.

$\varepsilon$ is the measurement uncertainty. For simplicity, IFEFFIT assumes that error is evenly distributed in $R$ space and so assigns the same measurement uncertainty to every data point. The default in
IFEFFIT is to calculate the root mean square value of the $\chi(R)$ spectrum between 15 and 25 Å.

![Graph showing theoretical and calculated EXAFS spectra](image)

**Figure 5-12** Theoretical-calculated EXAFS spectrum of well-known copper FCC crystal structure compared to EXAFS data of a copper foil. Upper: the real part of the data and fit; lower: the magnitude of the data and fit. Points: experimental data, lines: fitting.

Both the real and imaginary parts of the complex Fourier transforms of the data and theory are used, instead of the magnitude and phase. A fit to our copper metal data is shown in Figure 5-12. The misfit in the magnitude plot is always a factor of $\sqrt{2}$ bigger than the misfit in either the real or imaginary parts.
This is because the fit of the real or imaginary part (Figure 5-12) is less sensitive than the magnitude.

The minimization of the $\chi^2$ is performed by the Levenberg-Marquardt non-linear least squares minimization. The absolute misfit between theory and data can be calculated as

$$R = \sum_{i=1}^{N_{\text{en}}} \frac{[\text{Im}(\chi_{\text{data}}(R_i) - \chi_{\text{th}}(R_i))]^2 + [\text{Re}(\chi_{\text{data}}(R_i) - \chi_{\text{th}}(R_i))]^2}{[\text{Im}(\chi_{\text{data}}(R_i))]^2 + [\text{Re}(\chi_{\text{data}}(R_i))]^2}$$ (5-20)

For demonstration, a comparison of theoretical calculated EXAFS with FCC copper metal crystal structure and our experimental copper foil data in radial space is plotted in Figure 5-12. The fitting was performed between around 2 to 6Å.
Chapter 6  EXAFS Experimental Design

6.1  Apparatus Setup in MRCAT beamline at the Advanced Photon Source

All the EXAFS data of this study were collected in the Materials Research Collaborative Access Team (MRCAT) beamline at the Advanced Photon Source (APS) in Argonne National Laboratory.

\[ \frac{\Delta E}{E} \times 10^4 \text{ at } 10\text{keV} \]

*Peak brilliance @ 6.5keV: 9.6 \times 10^{18} \text{ ph/sec/mrad}^2/\text{mm}^2/0.1\%

*bw

**Figure 6-1**  Schematic representation of APS storage ring and Hutch A at MRCAT beamline.

The high intensity x-ray beam from the APS synchrotron storage ring is tuned by a Si (111) double crystal monochromator in Hutch A, as represented in Figure 6-1. The double crystal monochromator consists of a cryo-cooled first Si crystal and a 250mm long second Si crystal which provides an energy range of 4.8 keV to 30 keV from the Bragg reflection. The second crystal has a piezoelectric tuning actuator with acoustic coupling feedback. The energy
resolution of the tuned monochromic x-ray beam reaches $\Delta E/E \sim 10^{-4}$ at 10 keV. The peak brilliance was measured to be $9.6 \times 10^{18}$ ph/sec/mrad$^2$/mm$^2$/0.1% bw.

![Graph showing reflectivity vs. photon energy with labels for Cu K edge EXAFS scanning range, 2nd order harmonic reflection, and 3rd order harmonic reflection.](image)

**Figure 6-2** Computed reflectivity of rhodium at incident angle 89.64 degree.$^{94}$

The crystal monochromators provide output beams that contain unwanted harmonic energies since higher orders of diffraction are unavoidable in Bragg reflection. The presence of harmonics results in drastic errors in the amplitudes of the absorption coefficient which would alter EXAFS determined coordination numbers. Thus, a 60cm long flat harmonic rejection mirror with Pt and Rh coatings is used at the MRCAT beamline (Figure 6-3). At certain selective incident angles (usually large), the harmonic mirror is transparent to harmonic x-ray photons (high energy) but highly reflecting to the fundamental ones. The energy of the fundamental reflection range tuned by the double crystal monochromator for a Cu K-edge EXAFS scan is usually from 8800 through 9800 eV. As represented in Figure 6-2, the rhodium reflectivity in this range at an incident angle of 89.64° is approximately 0.8. However there is almost zero
reflection for higher order harmonic photons. Data in Figure 6-2 is theoretically computed with a model provided by the Center for X-ray Optics at Lawrence Berkeley National Laboratory. 94

EXAFS is a nondestructive technique particularly sensitive to the local lattice environment of an absorbing element in a material; in the case of this study the absorber was copper. For low concentrations of impurities in a material, the EXAFS signal can be enhanced through a high purity Ge multi-element x-ray fluorescence detector which provides good sensitivity to the ~0.3% Cu in our CdTe thin films.

**Figure 6-3** Apparatus arrangement in the experimental station – Hutch B at MRCAT beamline.

In the experimental station - Hutch B in MRCAT (Figure 6-3), the Cu K-edge EXAFS spectra of the Cu-doped CdTe samples were collected in fluorescence mode with the 13-channel high purity Ge detector, by setting a 600eV wide window at the position of the Cu Kα (8048 eV) peak in the fluorescence spectrum (Figure 6-4). Samples were always placed into the incident beam with an angle around 45°, with the Ge detector facing the sample
beside the beam. Reference materials of CuO, Cu$_2$O, CuCl, CuCl$_2$ and Cu$_2$Te powders were applied to the adhesive of several layers of Kapton tape and the absorption spectra were collected in the transmission mode with detection by the N$_2$ ion chamber (Transmitted Intensity Monitor).

![Figure 6-4](image.png)

**Figure 6-4** X-ray fluorescence spectrum of copper doped CdTe polycrystalline film excited by 9.5 keV photon flux.

### 6.2 Sample preparation

In this study, results were obtained on magnetron-sputtered CdTe films that were diffused with copper following the procedure used for creating a solar-cell back contact. Our EXAFS measurements identified the chemical environment of the majority of the copper and show major differences depending on whether the CdTe film has been treated with chloride prior to the Cu diffusion.
The data indicate that the Cu chemistry is strongly affected by the chloride treatments.

The 2-3 micron CdTe layers were magnetron sputtered at ~ 250 °C onto fused silica substrates. Some samples were selected for CdCl$_2$ vapor treatment, which was done at 387 °C in CdCl$_2$ vapor in a dry air environment (<10PPM water) for 30 minutes. Then all of the sputtered CdTe films, either with or without CdCl$_2$ treatment, were evaporated with 40Å Cu followed with diffusion. The Cu was diffused in N$_2$ at 150 or 200°C for at least 45 minutes. Some of the CdCl$_2$ treated samples were evaporated with 55Å Au layers following the Cu deposition without vacuum break as back contact fabrication for complete cell structure. These samples were deposited with both copper and gold layers in order to prepare the polycrystalline CdTe film in the condition as close as possible to the one in functional solar cells.

Cu K-edge EXAFS data were then collected from both chloride-treated and untreated samples. We also selected a fraction of these Cl-treated samples for short 5% hydrochloric acid etching with the purpose of removing the metallic copper left on the film surface. However, dissolution of Cu$_2$O in Cl-treated polycrystalline CdTe film was observed. More details will be discussed in Chapter 8.

Based on our observation of the instability of Cu$_2$O in the chloride-treated CdTe film, we also selected one of the chloride-treated films for a long-period heating. The long heating process was carried out in a pure N$_2$ atmosphere for 4.5 hours at 200 °C rather than 45 minutes as for the diffusion of other samples.
Figure 6-5  Measurement of absorption length of polycrystalline CdTe in the x-ray photon energy range of 8.8~10.1 keV.

Fused silica, instead of regular soda lime glass, was chosen as the substrate material to avoid contaminating signals from residual copper and other heavy elements in regular glasses. Our measurement of the attenuation length of 8.8~10.1 keV x-ray photons through a series of sputtered CdTe films on polyimide tape indicates that over 60% of these x-ray photons pass through the
~2 μm CdTe films into the substrates, where most of the absorption is due to Te and Cd L-shell absorption.

The measurement of the attenuation length (inverse of the linear absorption coefficient, $d_0 \equiv 1/\mu$) is represented in Figure 6-5. The relatively high noise level at the high photon energy side is mostly due to the decrease of incident x-ray beam intensity, as plotted in Figure 6-6.
Chapter 7  Effect of CdCl₂ Treatment on the Copper Local Structure

7.1  Qualitative Analysis

In this chapter, we will discuss extended x-ray absorption fine structure (EXAFS) results obtained on magnetron-sputtered CdTe films that were diffused with copper following the procedure used for creating a cell back contact. The experimental methodology has been described in detail in Chapter 6.

Our EXAFS measurements identify the chemical environment of the majority of the copper and show major differences depending on whether the CdTe film has been treated with chloride prior to the Cu diffusion. The data indicate that the Cu chemistry is strongly affected by the chloride treatments.

The most important result of this study is the finding that Cu-doped CdTe films that have not undergone CdCl₂ treatment have absorption edge structure similar to Cu₂Te. However, films that received a CdCl₂ treatment prior to Cu diffusion show features similar to Cu₂O and CuO.

As shown in Figure 7-1, comparison with reference materials in the X-ray Absorption Near Edge Structure (XANES) region usually helps to understand the predominant chemical bonds surrounding the core atoms in unknown samples. Before CdCl₂ treatment all of the CdTe films are observed to have features similar to Cu₂Te (Figure 7-1a). However, the films with CdCl₂ treatment show features most similar to Cu₂O and CuO (Figure 7-1b). Note that the absorption amplitude
Figure 7-1 XANES spectra: a) Non-chloride treated CdTe films with diffused copper show features similar to Cu₂Te; b) chloride-treated CdTe films with diffused copper show features similar to Cu₂O and CuO.

depends on the sample thickness in direct transmission measurements and depends on detector efficiency, Cu concentration and sample thickness of the
CdTe:Cu films when fluorescence detection was used. For convenience of comparison, absorption curves in relative magnitude are plotted in Figure 7-1.

As discussed in Chapter 5, EXAFS can be extracted from the x-ray absorption spectra by removing the background. The x-ray absorption backgrounds are calculated as x-ray absorbance in the sample without the electron scattering by neighbor atoms. The EXAFS function in $k$ space, $\chi(k)$, is then derivable through the background subtraction process. Finally, the $\chi(k)$ function is Fourier transformed into radial space - $\chi(R)$, which is called the phase-uncorrected radial distribution function of EXAFS.\(^9\) Our analyses were performed through IFEFFIT, an interactive program for EXAFS analysis.\(^1\)

The $\chi(R)$ functions for the two cases - with and without CdCl$_2$ treatment - are shown in Figure 7-2. In the copper-diffused but non-chloride treated film (Figure 7-2a) the $\chi(R)$ closely follows that of a Cu$_2$Te reference spectrum except for the peak heights. The magnitude of $\chi(R)$ depends on the coordination number in the corresponding neighbor shell (see discussion later for Table 7-1 and Table 7-2). In addition, the strongest peak at 2.42 Å shifts to slightly shorter values by about 0.1 Å than for cuprous telluride. Further study of this shift will be discussed in Section 7.2.1 in the theoretical \textit{ab initio} multiple-scattering modeling with a standard computer code FEFF.\(^1\)

For the CdCl$_2$ treated films, the shape of the $\chi(R)$ and the position of the peaks are substantially changed from that of the non-chloride-treated films. Thus, we infer that the chemical environment of the majority of the copper atoms is substantially different when diffused after chloride treatment. The first primary
Figure 7-2  The phase-uncorrected radial distribution function, $\chi(R)$, of Cu diffused CdTe film without a) and with b) and c) prior CdCl$_2$ treatment.
peak resides at a position quite different from that of cuprous telluride, Cu$_2$Te, or of cupric chloride, CuCl$_2$. It also differs from that of CuCl which has a $\chi(R)$ structure similar to that of CuCl$_2$ (Figure 7-2c). However the $\chi(R)$ of the chloride-treated CdTe film corresponds closely to that of cuprous oxide, Cu$_2$O, with the first peak at 1.50 Å, as shown in Figure 7-2b. The $\chi(R)$ is not consistent with the existence of bulk Cu$_2$O inclusions in the film since the second nearest-neighbors of copper in cuprous oxide are copper atoms. The absence of the second-nearest-neighbor peak at 2.82 Å of Cu$_2$O, shown in Figure 7-2b, suggests that we are not seeing nano-crystal inclusions of cuprous oxide but rather copper-oxygen pairs formed in the film or quite likely along the grain boundaries. (See further discussion in Section 8.3)

7.2 FEFF Fitting

7.2.1 CdTe:Cu film without CdCl$_2$ treatment

In the as-deposited, Cu-diffused polycrystalline CdTe film, FEFF fitting of the first and second dominant peaks in the phase-uncorrected radial distribution function $\chi(R)$ (Figure 7-1), indicates Te and Cu shells surrounding the absorbing Cu atom. This shows that the predominant Cu environment is similar to Cu$_2$Te. These Cu-Te and Cu-Cu bonds were observed in all the copper-diffused CdTe films independent of the history of the films, with or without chloride-treatment and under etching or any stressed condition. The previous EXAFS work by Soo et al. on copper-diffused CdTe single crystals found no evidence of Cu$_2$Te. This suggests that the Cu$_2$Te in polycrystalline CdTe films may be located at the surface and the grain boundaries.
Figure 7-3  FEFF fitting to Cu$_2$Te reference. Fine line: experimental data of Cu$_2$Te reference. Thick line: theoretical fitting. The left inset (plotted by crystal and molecular structure visualization computer software) is the local structure of Cu atoms in the reference model. The right inset shows the near-neighbor atoms around a Cu atom as the center (plotted with a little bigger size than other Cu atoms). There are: one Cu neighbor atom located at distance of 2.33Å, three Cu neighbor atoms at distance of 2.45Å and three Te neighbor atoms at distance of 2.67Å. These three nearest-neighbor shells contribute to most of the scattering amplitude - $\chi(R)$ as indicated by the FEFF fitting.

<table>
<thead>
<tr>
<th>Scattering path</th>
<th>N</th>
<th>R(Å)</th>
<th>dR(Å)</th>
<th>$\sigma^2 (10^{-3} \text{ Å}^2)$</th>
<th>$\Delta E_o$(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-Cu (1nn)</td>
<td>0.2 ± 0.1</td>
<td>2.26 (fixed)</td>
<td>-0.07</td>
<td>1.9 ± 6.6</td>
<td></td>
</tr>
<tr>
<td>Cu-Cu (2nn)</td>
<td>0.9 ± 0.2</td>
<td>2.53 ± 0.03</td>
<td>0.09</td>
<td>4.3 ± 16.1</td>
<td>6.1 ± 2.6</td>
</tr>
<tr>
<td>Cu-Te (3nn)</td>
<td>2.6 ± 0.7</td>
<td>2.66 ± 0.08</td>
<td>-0.01</td>
<td>22.5 ± 8.0</td>
<td></td>
</tr>
</tbody>
</table>

(Note: 1. N ~ coordination number, R ~ physical bond length, dR ~ bond length shift from theoretical structure, $\sigma^2$ is the mean square disorder, $\Delta E_o$ is overall threshold $E_o$ (Cu absorption k edge) shift; 2. Scattering path Cu-Te means single scattering of electron by Te atom back to Cu core atom) 3. 1nn means the 1st nearest-neighbor, 2nn is 2nd nearest-neighbor, 3nn is 3rd nearest-neighbor.)
Cu$_2$Te crystal structure is often observed to have many complex phases strongly depending on the growth processes.\textsuperscript{105,106,107,108} In this study, a hexagonal *high-temperature* structure which was first suggested by Novotny\textsuperscript{109} is used to fit the EXAFS data of a Cu$_2$Te reference (Figure 7-3 and Table 7-1). The structure of Cu$_2$Te proposed by Novotny was examined at around 800 °C. But our spectrum was taken at room temperature. The unit cell of this crystal structure has: $a = b = 4.237$ Å, $c = 7.274$ Å. Atomic positions are represented in the point group D$_{6h}^1$: Cu: (1/3, 2/3, 0.16), Te: (0, 0, 0.306).\textsuperscript{110} The local structure of Cu atom in this model is plotted in the insets of Figure 7-3. Three single scattering (SS) paths contribute most to the $\chi(R)$. From the Cu$_2$Te structure proposed by Novotny, the neighboring shells around the copper core atom of these three paths are derivable to be: 1) the Cu shell at 2.327 Å with coordination number (N) of 1; 2) the Cu shell at 2.446 Å with N = 3; 3) the Te shell at 2.667 Å with N = 3. The fitting to reference spectrum only deduces the neighbor distance and coordination number of the neighbor shells rather than determine the crystal structure as no bond angles are obtain in EXAFS.

The single scattering (SS) paths of 2$^{nd}$ and 3$^{rd}$ nearest-neighbor shells (Cu and Te) were then fitted to the EXAFS of the as-deposited CdTe:Cu film (Figure 7-4) by fixing the mean square fluctuation parameter $\sigma^2$ of both shells the same as the ones in Cu$_2$Te reference. The FEFF fitting does verify that the Te neighbor shell shifts to shorter distance in the as-deposited film compared to the Cu$_2$Te reference, as observed in Figure 7-2a. Fitting results (Table 7-2) indicate that the Cu neighbor shell is located at 2.51Å from copper core atoms, the same
distance as in the Cu$_2$Te reference (Table 7-1) within the fitting error, and with the same coordination number. The shift is due to the shorter path length of the Te shell as 2.57Å. Because of the strong interference between the $\chi(R)$ of Te and Cu shells as discussed in the latter part of this section, both peaks shift to shorter distance. However, the 1$^{st}$ nearest-neighbor of Cu$_2$Te, Cu shell at 2.26Å (Table 7-1), is excluded in the fitting as discussed below.

![Image of EXAFS](image.png)

**Figure 7-4** The $\chi(R)$ functions of Cu K-edge EXAFS of copper diffused as-deposited CdTe polycrystalline film. Fine lines: experimental data, thick lines: theoretical fitting.

<table>
<thead>
<tr>
<th>Table 7-2</th>
<th>FEFF fitting results on parameters of local structure surrounding Cu atoms in as-deposited CdTe film. (Note: refer to Table 7-1 for definition)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scattering path</td>
<td>N</td>
</tr>
<tr>
<td>Cu-Cu (2nn of Cu$_2$Te)</td>
<td>0.9 ± 0.2</td>
</tr>
<tr>
<td>Cu-Te (3nn of Cu$_2$Te)</td>
<td>3.9 ± 1.0</td>
</tr>
</tbody>
</table>
A plausible explanation to the fitting is the small amount of Cu in the film. As mentioned before, Cu is a fast diffuser in CdTe, particularly along the grain boundaries. Meanwhile, the appearance of Cu$_2$Te in the polycrystalline CdTe film but not in crystalline CdTe suggests that the Cu most likely is located at the surfaces of grain boundaries in CdTe film. Given the 40Å of Cu that is deposited and diffused into the 2μm thick CdTe film with 0.5μm grain size, it is readily shown that on average, there is only enough Cu to provide a 2.6Å Cu layer covering all the surfaces of grain boundaries if one were to assume that the Cu layer covers all the surface area uniformly. It is likely that the grain boundary Cu will be thicker near the back contact. But on most surfaces of grain boundaries, Cu atoms should be only enough to cover as monolayer. The 1$^{\text{st}}$-nearest-neighbor of the Cu$_2$Te reference is a Cu atom from another Cu layer (see inset of Figure 7-3; in the proposed model, the path length is 2.33 Å). In the CdTe film discussed here, it is likely that the secondary Cu layer does not exist due to insufficient Cu in the film. Meanwhile, in other samples we are going to study later in this dissertation, the amounts of copper diffused into the films are the same as this sample. The 1$^{\text{st}}$-nearest-neighbor shell (Cu) of Cu$_2$Te is also excluded in the fittings to EXAFSs of those samples, which also could be understood by the inexistence of a secondary Cu layer.

It should be mentioned that dangling bonds of Te atoms on the surface of CdTe grain boundaries are able to attract the Cu atoms. The surface of a grain boundary is usually not as flat as the Te plane in Cu$_2$Te crystal (see inset in Figure 7-3) but disordered. The valleys of grain boundary surface with lower potential
energy, in other words more available Te dangling bonds, could be where the Cu atoms tend to reside. If this is true in the as-grown CdTe film, then the relatively larger coordination number (N=3.9) of the Te shell from the FEFF fitting to EXAFS of this sample than in Cu₂Te reference (N=2.6) might be explained by more available Te in the valleys of the grain surfaces to be bound with Cu. As to the smaller Cu-Te bond length (Table 7-1 and Table 7-2), it might be understood as due to the compression from the wall of Te valleys.

It is also necessary to mention that a multi-shell analysis is performed for the copper telluride structure studied above. As discussed in Chapter 5, when two shells are not truly isolated, they often interfere with one another. This interference often reduces the apparent $\chi(R)$ amplitude where the two peaks are overlapping and appears as a sharp minimum. The major indication of interference is that the peaks are generally asymmetrical. As one can notice in both Figure 7-2a and Figure 7-4, the sharp minimum and asymmetrical peak shape appear in the $\chi(R)$ of the as-deposited CdTe:Cu film. In this case, an inverse Fourier transform is then necessary to verify whether the two peaks are isolated enough.

By selecting the r-window (a rectangular function) range of the inverse transform, the two peaks of $\chi(R)$ at 1.90 and 2.42 Å are separately transformed back to k space. Comparing with the $\chi(k)$ structure as shown in Figure 7-5b and c, the individual inverse transforms of these two peaks do not prove either of them an apparent component of the $\chi(k)$. This indicates that the two peaks interfere strongly with each other, as demonstrated in Figure 7-5. Thus single-shell
Figure 7-5  Inverse Fourier transform with different r-window ranges: (a) 1.6 ~ 2.75 Å, covering both peaks, the inverse transform of which in k space matches most of the oscillation structure of data; (b) 1.6 ~ 2.2 Å, inverse transform of the peak at shorter distance obviously shows different oscillation frequency from the data; (c) 2.2 ~ 2.75 Å, inverse transform of the peak at further distance, even though in k space its oscillation frequency follows closely the χ(k) structure, the oscillation amplitude does not match. Note: figures on left are χ(R) - the forward Fourier transformed EXAFS function and the selected r-window range, corresponding inverse transform and χ(k) of data are compared on right side.
analysis, which fits the $\chi(R)$ function with shells one by one, is not proper for either of these two peaks. The two peaks have to be analyzed together in the FEFF fitting. Multi-shell analysis, fitting the two copper shells and one Te shell simultaneously to the two peaks, is performed for both the Cu$_2$Te reference and as-deposited CdTe:Cu films. Since Cu$_2$Te appears in all of the copper-diffused CdTe films in this study in spite of the treatment carried out on the films, the multi-shell analysis is also performed for other films discussed later to fit the similar copper telluride structure.

7.2.2 CdTe:Cu film with prior CdCl$_2$ treatment

![Figure 7-6](image)

**Figure 7-6** FEFF fitting to a Cu$_2$O reference. Fine line: experimental data of Cu$_2$O reference. Thick line: theoretical fitting. The inset is the local structure of Cu atom in the reference model, which shows around the central Cu atom (plotted with a little bigger size than other Cu atoms) there are two O neighbor atoms located at 1.85Å and twelve Cu neighbor atoms at distance of 3.02Å.

Cu$_2$O has a high-symmetry, cubic structure with the lattice constant of unit cell $a = 4.2696$ Å. Atoms are in the special positions of point group $T_d^2$: Cu:
(1/4, 1/4, 1/4), O: (0, 0, 0). The structure employed in the fitting to the Cu₂O reference was shifted by (-1/4, -1/4,-1/4) to reside the origin on a Cu atom for better results. The local structure of Cu atom in this model is plotted in the inset of Figure 7-6. The single scattering (SS) path with path length 1.839 Å contributes to the first primary peak at 1.47 Å in χ(R). From the proposed Cu₂O structure given by Wyckoff, the nearest-neighbor shell around the copper core atom is an oxygen shell at 1.849 Å with coordination number N = 2.

Table 7-3 FEFF fitting results on parameters of Cu₂O. (Note: refer to Table 7-1 for definition)

<table>
<thead>
<tr>
<th>Scattering path</th>
<th>N</th>
<th>R(Å)</th>
<th>dR(Å)</th>
<th>σ²(10^{-3} Å²)</th>
<th>ΔE₀(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-O (1nn)</td>
<td>1.5 ± 0.4</td>
<td>1.84 ± 0.01</td>
<td>-0.01</td>
<td>1.5 ± 0.8</td>
<td>8.3 ± 1.7</td>
</tr>
<tr>
<td>Cu-Cu (2nn)</td>
<td>20.2 ± 5.1</td>
<td>3.04 ± 0.02</td>
<td>0.02</td>
<td>27.7 ± 4.4</td>
<td></td>
</tr>
</tbody>
</table>

In the case of CdTe films that were CdCl₂ treated and then deposited and diffused with copper (Figure 7-7), the predominant peak is identified as surrounding oxygen shells with coordination number of 1.6 at a distance 1.89 Å. This is consistent with the nearest-neighbor distance in Cu₂O crystals. The mean square fluctuation parameter - σ² of the oxygen shell is fixed the same as the ones in the Cu₂O reference in the fitting. Since neither of the second- and third-nearest-neighbor peaks correspond closely to the second-nearest-neighbor in Cu₂O which is a Cu atom shell(Table 7-3), the data suggest that Cu impurities do not form microcrystalline Cu₂O inclusions, but probably Cu₂O monolayer.

The fitting indicates that the other two peaks in the phase-uncorrected
radial distribution function (see in Section 5.2.2.4 for definition), $\chi(R)$, at 2.06 and 2.61 Å, respectively, arise from the Cu and Te shells at distances of 2.57 and 2.66 Å similar to the as-deposited films except for 0.06 Å and 0.09 Å distortions, respectively (see Table 7-2 and Table 7-4). The mean square fluctuation parameters - $\sigma^2$ of both shells are also fixed the same as the ones in Cu$_2$Te reference in the fitting. The copper shell at distance 2.57 Å generates the peak

![ CdCl$_2$ treated CdTe:Cu ](image)

**Figure 7-7** The $\chi(R)$ functions of the Cu K-edge EXAFS of the copper diffused CdCl$_2$ treated CdTe film. Fine lines: experimental data, thick lines: theoretical fitting.

**Table 7-4** FEFF fitting results on parameters of local structure surrounding Cu atoms in CdCl$_2$ treated CdTe film.

<table>
<thead>
<tr>
<th>Scattering path</th>
<th>N</th>
<th>R(Å)</th>
<th>dR(Å)</th>
<th>$\sigma^2$(10$^{-3}$ Å$^2$)</th>
<th>$\Delta E$_o(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-O (1nn of Cu$_2$O)</td>
<td>1.6 ± 0.4</td>
<td>1.89 ± 0.01</td>
<td>0.04</td>
<td>1.5 (fixed)</td>
<td></td>
</tr>
<tr>
<td>Cu-Cu (2nn of Cu$_2$Te)</td>
<td>0.2 ± 0.1</td>
<td>2.57 ± 0.04</td>
<td>0.13</td>
<td>4.3 (fixed)</td>
<td>9.7 ± 1.4</td>
</tr>
<tr>
<td>Cu-Te (3nn of Cu$_2$Te)</td>
<td>1.9 ± 0.5</td>
<td>2.66 ± 0.04</td>
<td>-0.01</td>
<td>22.5 (fixed)</td>
<td></td>
</tr>
</tbody>
</table>
at 2.06 Å in χ(R) (see Section 5.2.2.4 for explanation), with a coordination number 0.2. While the peak at 2.61 Å in χ(R) arises from tellurium shell 2.66 Å away from the core copper atom and with coordination number 1.9. Within the error range of the fitting, the two Cu and Te shells are at the same distance from the core copper atom like in the Cu₂Te reference (Table 7-1), except for smaller coordination numbers than either the as-deposited one or the Cu₂Te reference. This suggests most copper atoms in the chloride-treated film tightly bind to oxygen forming a Cu-O bond within the nearest-neighbor range. Meanwhile a small portion of the copper in the film binds to tellurium atoms forming copper telluride. Given the small total amount of diffused copper atoms, the amount of copper bound to tellurium is even smaller and there may be no copper atom planes formed as in the Cu₂Te crystal (see the inset in Figure 7-3). But there could still be a very small number of copper atoms residing in some of the tellurium valleys on the grain boundary surfaces binding to tellurium dangling bonds. In this case, the compression from the wall of valleys is weak. This might explain the same bond lengths of the Cu-Cu and Cu-Te bonds as in the Cu₂Te reference, as well as the smaller coordination number of the Cu and Te neighbor shells.

It is worth pointing out that as mentioned before, on some of the CdCl₂-treated CdTe polycrystalline films, we deposited 55 Å of Au immediately after Cu evaporation (without vacuum break) in order to help protect the copper on the film surface from oxidization by air. The EXAFS data from this film yielded a similar Cu₂O signature indicating it is not simply oxidization by the air. I propose there is a pre-oxidized environment in the film formed during the chloride
treatment and when the copper layer is deposited and diffused, most of the copper atoms react and bind with pre-existed oxygen atoms in the film due to the chloride treatment in air.

7.3 Discussion

Due to the requirement for a high work function metal, it has been proven to be challenging to form a low resistance ohmic contact in CdTe cells. Now the most common strategy is to form a Te-rich surface by selective chemical etching before applying copper or material with a copper component.\textsuperscript{113} It has been directly measured at the back surface by GIXRD methods\textsuperscript{114} that copper will react with tellurium to form a $p^+$ layer of Cu$_2$Te, which is then contacted with a secondary metal layer or graphite.

However, for sputtered CdTe cells fabricated in the UT PV group, 14% operation efficiency has been accomplished, even without applying chemical etching to form a Te-rich surface on the CdTe layer before copper and gold deposition. Our observations of copper telluride in all of the copper-diffused CdTe films, independent of the treatment performed on the film, may indicate a benefit of the \textit{sputtering-deposition} of CdTe film that during diffusion, copper tends to bind with tellurium and form Cu$_2$Te most likely at the back surface and grain boundaries. These observations help to explain the high performance of \textit{sputtered} CdTe cells even with the absence of the formation of a Te-rich surface during fabrication.

Our films were diffused, and if one were to assume uniform distribution of Cu through out the CdTe, the average concentration of copper would be 0.3% or
an average density would be $1-2 \times 10^{20} \text{ cm}^{-3}$ (see Appendix B). However, capacitance-voltage (C-V) measurements on typical CdTe solar cells, including our sputtered cells, indicate a typical doping concentration of holes of a few times $10^{14} \text{ cm}^{-3}$. Secondary ion mass spectroscopy (SIMS) on some CdTe cells has shown Cu atomic concentrations of a few times $10^{19} \text{ cm}^{-3}$. Our preparation of films was done with evaporated Cu amounts that were only slightly higher than we use for cell fabrication. Clearly much Cu is not active as an acceptor in these films and there is considerable interest in where the non-electrically active Cu is located.

Based on our x-ray absorption fine structure measurements, we conclude that the answer depends entirely on whether the film has received the typical treatment with CdCl$_2$. Thus, films which received the Cu diffusion having no prior treatment with CdCl$_2$ appear to show the Cu mostly bound with Te similar to Cu$_2$Te. However, if the film has received the CdCl$_2$ treatment, which for cell-fabrication is always done in the presence of some O$_2$, then most Cu appears to be bound with neither Cl nor Te but with O. The most plausible interpretation is that most of the copper was available at the back surface and grain boundaries where it could easily be oxidized by oxygen introduced during the prior CdCl$_2$ treatment. I will provide further results supporting this interpretation in Chapter 8. Note that it is generally understood that this CdCl$_2$ treatment is important for passivating the grain boundaries and thus is a critically important step in the fabrication of high efficiency polycrystalline thin-film solar cells. These x-ray
absorption fine structure measurements point toward a plausible interpretation of why this chloride treatment is important for fabricating high efficiency cells.¹¹⁶
Chapter 8  Instability of Cu$_2$O in Polycrystalline CdTe Thin Film

8.1  Location of the Cu$_2$O

8.1.1  Indirect Evidence from the Solubility Cu$_2$O in HCl acid

We believe that the most plausible structure that can explain the observations of Cu$_2$O in chloride-treated CdTe:Cu film is one which has the grain surfaces as the major repository of copper, with the copper bound in a nearest-neighbor environment very similar to that of Cu in Cu$_2$O. It has almost always been observed that polycrystalline CdTe deposited on CdS in a functional cell forms a “cylindrical” structure as represented in Figure 8-1, with grain size from

![Figure 8-1](image)

**Figure 8-1**  TEM cross-sections of CdTe films showing the cylindrical grain structure of polycrystalline CdTe (from Al-Jassim, et al, reference 117).
Figure 8-2  a) $\chi(R)$ of CdTe:Cu with prior chloride treatment etched by 9% HCl acid for 10 seconds (thick line) and chloride-treated CdTe:Cu film (broken line); b) the same HCl etched CdTe:Cu film with prior CdCl$_2$ treatment (thick line) and non-treated CdTe:Cu (fine line).

several tenths of microns to a couple of microns depending on the deposition method. With this model, a straightforward estimate of the amount of copper available from a 3 nm layer and a 2.5 $\mu$m thick CdTe film having ~0.5$\mu$m diameter$^{118}$ "cylindrical" grains extending through the film indicates just enough
Cu to provide approximately a monolayer coating of the grains. However, in the case of real film, the copper oxide could only cover part of the grain surfaces.

Etching experiments provided an additional consistency check of this model. We found that the XAFS features similar to Cu$_2$O in the CdCl$_2$-treated CdTe films are removable by selective etching.

We chose several chloride-treated and copper diffused CdTe films for selective HCl etching right before the EXAFS data collection. There was no Au layer deposited on the top surface to avoid a possible barrier to chemical etching. As shown in Figure 8-2a, after 10 seconds of etching in 9% HCl, the peak at 1.50Å is gone. Post etching, the two major peaks at 1.90 and 2.39 Å in $\chi(R)$ suggest that most of the remaining copper is found to be bound with Cu and Te atoms as in non-chloride-treated CdTe films (Figure 8-2b).

![Figure 8-3](image)

**Figure 8-3** The $\chi(R)$ functions of Cu K-edge EXAFS of copper diffused CdCl$_2$ treated CdTe film etched with in 9% HCl acid for 10 seconds. Fine lines: experimental data, thick lines: theoretical fitting.
Table 8-1  FEFF fitting results on parameters of local structure surrounding Cu atoms in CdCl$_2$ treated CdTe film followed by HCl etching.  (Note: refer to Table 7-1 for definition)

<table>
<thead>
<tr>
<th>Scattering path</th>
<th>N</th>
<th>R (Å)</th>
<th>dR(Å)</th>
<th>$\sigma^2(10^{-3} \text{ Å}^2)$</th>
<th>$\Delta E_o$(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-O (1nn of Cu$_2$O)</td>
<td>0.5 ± 0.1</td>
<td>2.09 ± 0.03</td>
<td>0.24</td>
<td>1.5 (fixed)</td>
<td></td>
</tr>
<tr>
<td>Cu-Cu (2nn of Cu$_2$Te)</td>
<td>0.9 ± 0.2</td>
<td>2.49 ± 0.01</td>
<td>0.04</td>
<td>4.3 (fixed)</td>
<td>-0.7 ± 1.5</td>
</tr>
<tr>
<td>Cu-Te (3nn of Cu$_2$Te)</td>
<td>5.1 ± 1.3</td>
<td>2.53 ± 0.03</td>
<td>-0.14</td>
<td>22.5 (fixed)</td>
<td></td>
</tr>
</tbody>
</table>

The FEFF fitting (Table 8-1) indicates that the two peaks at 1.90 and 2.39Å in the $\chi(R)$ function (Figure 8-2 and Figure 8-3) arise from the 2$^{nd}$ and 3$^{rd}$ nearest-neighbor shells (copper and tellurium, respectively) of Cu$_2$Te, but the 1$^{st}$ nearest-neighbor shell (copper at 2.27 Å) of Cu$_2$Te is also excluded in the fitting as the as-grown CdTe films discussed in Section 7.2.1.  The fitting indicates the copper and tellurium shells reside at distances of 2.49 Å and 2.53 Å, respectively.  Both shells shift to shorter distance than in either Cu$_2$Te or as-grown CdTe film (Table 7-1 and Table 7-2).  The coordination number of the copper shell (N = 0.9) is the same as in Cu$_2$Te within the fitting error.  However the coordination number of the tellurium shell (N = 5.1) is almost double of the one in Cu$_2$Te (N = 2.6 in Table 7-1).  A plausible explanation will be discussed in the later part of this section. The shoulder at 1.5 Å in the $\chi(R)$ function (Figure 8-2) and the higher intensity of the 1.9 Å peak than the non-treated film (Figure 8-2b) arises from oxygen as evidence of Cu$_2$O remaining after the HCl etching.  The fitting indicates the path length of this oxygen shell is larger (R = 2.09 Å) than the same shell in Cu$_2$O (R = 1.84 Å) or even the 1$^{st}$ nearest oxygen shell in CuO (R = 1.94 Å,
And the coordination number of this oxygen shell is only 0.5. The mean square fluctuation parameters - $\sigma^2$ of all the shells are fixed the same as the ones in corresponding references ($\text{Cu}_2\text{Te}$ and $\text{Cu}_2\text{O}$) in the fitting.

Considering the dissolution of $\text{Cu}_2\text{O}$: $\text{Cu}_2\text{O} + 2\text{H}^+ \rightarrow \text{H}_2\text{O} + 2\text{Cu}^+$, and other oxides (such as $\text{CdO}$, $\text{CdTeO}_3$, $\text{CdTe}_2\text{O}_5$, $\text{TeO}_2$ and $\text{Te}_2\text{O}_5$) possibly occurring during HCl etching, most of the oxygen could have been removed by the acid but there is likely to be a small portion remaining in the film given the short period etching (10 seconds). There may be too little oxygen in the film to form the monolayer $\text{Cu}_2\text{O}$. The oxygen remaining in the film could be shared by copper and other elements most likely at the grain boundaries and surface of the film. The reduced copper atoms are then likely to bind with Te or nearby copper forming copper telluride as in $\text{CdTe}:\text{Cu}$ film without Cl treatment. However, it should be emphasized that the film morphology changes during the chloride treatment. For a sputtered CdTe film, recrystallization usually occurs during the treatment, which results in grain coalescence and closer packing. The inter-grain space might be smaller than in non-treated films. If this is true, a plausible explanation to the large coordination number (5.1) of the Te shell could be that the reduced copper atoms diffuse to areas of the grain surfaces, where there are more tellurium dangling bonds available. In this case, a sandwich structure of Te-Cu-Te atom planes, instead of the Te-Cu-Cu-Te structure as in the $\text{Cu}_2\text{Te}$ reference (see the inset in Figure 7-3), may form at such grain surface area. This could result in the doubled coordination number of the Te neighbor shell in
this sample. Also, the shorter path lengths of Cu and Te shells could also be explained by the compression from the grains at such area in this model.

However, another explanation of the larger coordination number of the tellurium shell could arise from an improper crystal structure of copper telluride as a standard in the fitting, since we used the high temperature structure given by Novotn¹⁰⁹ for the Cu₂Te EXAFS analysis. However, Novotn’s structure is the only available structure presently.

Also FEFF fitting suggests a small portion of copper binds with O consistent with the nearest-neighbor in Cu₂O (Table 8-1), yielding the higher intensity of the 1.90 Å peak and the shoulder at 1.50 Å (Figure 8-2b). This proves the existence of Cu₂O in the film before HCl etching and the small amount of Cu₂O after etching.

![Figure 8-4](image)

**Figure 8-4**  Schematic representation of the suspected location of Cu₂O at back surface and grain boundaries of a polycrystalline CdTe film.

After all, the significance of this EXAFS on the HCl etched, chloride-treated, CdTe:Cu film is that both experimental and theoretical fitting results (Figure 8-2, Figure 8-3 and Table 8-1) indicate that, after etching, the remaining copper is mostly bound to Te and Cu in the Cu₂Te structure with only small fraction
bound to oxygen. This is consistent with the much faster etch rate of Cu$_2$O compared with Cu$_2$Te in HCl. Concerning the short period of HCl etching which is not more than 10 seconds, I suggest this is indirect evidence that Cu$_2$O is primarily located along grain boundaries and the back surface of the CdTe film (Figure 8-4) where it can be dissolved quickly by hydrochloric acid. More discussion on the significance of this model will be given later (Section 8.3).

### 8.1.2 Direct Evidence from Back Contact Peel Off Process

Even though the EXAFS on the HCl-etched samples provides indirect evidence on the location of Cu$_2$O, some further proof is needed. By taking advantage of the facilities at MRCAT, we found the x-ray fluorescence studies to be a fast and convenient method for this purpose since the fluorescence intensity is proportional to the total amount of Cu atoms exposed to the excitation beam.

We prepared 0.13 μm CdS and 2.3 μm CdTe films sputtered on fused silica, followed by the standard CdCl$_2$ treatment, then 35 Å Cu and 200 Å Au deposition (Figure 8-5b). The samples were then heated at 150 °C for 45 minutes in ambient air to diffuse the copper into the CdTe. A layer of LOCTITE Quick Set Epoxy (Recorder TM-51 81502), usually several millimeters thick, was then hardened on the surface of the metal layer to separate the Au layer from the CdTe film at the interface.

The Cu $K_{\alpha}$ fluorescence intensities from peeled off Au layer (dashed line) and the remaining CdS/CdTe films (dotted line) are compared with the one from the film before Au/CdTe separation (solid line), as shown in Figure 8-5a. The x-ray fluorescence intensities prove that approximately 90% of the Cu remains at
Figure 8-5 a) Solid line: X-ray fluorescence of CdS/CdTe film with Cu/Au metal layer (sample A), dotted line: CdS/CdTe films without metal layer (sample B) and dashed line: the peeled off Au layer (sample C); b) the schematic structures of the samples. Note: the intensity of Cu K\(_{\alpha}\) fluorescence peak at 8048 eV is proportional to the total amount of Cu exposed under the x-ray beam (10 keV).

the back surface and about 10% is located in the CdTe film. The ~90% Cu peeled off with the Au layer by epoxy indicates that even after the diffusion, most
of the Cu actually locates at the interface of the Au layer and CdTe film.

More discussion on the significance of the location of the Cu$_2$O will be provided later in Section 8.3.

8.2 Transformation of Cu$_2$O to CuO

To understand the stability of Cu$_2$O layers in polycrystalline CdTe, we heated one of the chloride-treated films in flowing N$_2$ for 4.5 hours at 200 °C rather than 45 minutes as in other samples.

The shapes of the $\chi$(R) peaks are substantially changed (Figure 8-6a), especially the first primary peak. This suggests a substantial change in chemical environment of the majority of the copper. Since the peak position does not change significantly, the peak shape change should arise from the shell structure difference. Different species in the same neighbor shell always have a slightly different path length and have significant difference of peak positions in $\chi$(R). A qualitative comparison of $\chi$(R) of this sample with CuO indicates the first primary peak at 1.53 Å arising from an oxygen shell consistent with the first and second-nearest-neighbors of O in CuO, as shown in Figure 8-6b.

Cupric oxide, CuO, as the mineral tenorite has a structure with square coordination around the metal atom.\textsuperscript{121} A structure proposed by Asbrink and Norrby\textsuperscript{122} was used in this study, which is monoclinic with cell dimensions: $a = 4.684$, $b = 3.423$, $c = 5.129$, $\beta = 99.54^\circ$. The proposed atomic arrangement based on the point group C$_{2h}$\textsuperscript{6} has its atoms in positions: Cu (1/4, 1/4, 0), O (0, 0.4184, 1/4). The local structure of Cu atom in this model is plotted in the inset of Figure 8-7. From the CuO structure proposed by Asbrink and Norrby, the
nearest-neighbor shell around the copper core atom is an oxygen shell at 1.95 Å with coordination number \( N = 4 \) and the 2\(^{nd}\) nearest one is also oxygen shell at 2.78 Å with \( N = 2 \). The FEFF fitting to the EXAFS of the CuO reference (Table 8-2) indicates that the single scattering (SS) paths with path lengths 1.944 Å and 2.545 Å contributes to the first primary peak at 1.534 Å in \( \chi(R) \) (Figure 8-7).

Figure 8-6  Qualitative comparison of the copper diffused, chloride treated and long duration heated CdTe film (a) to CdCl\(_2\) treated CdTe:Cu with regular heating, and (b) to CuO and Cu\(_2\)Te.
Figure 8-7  FEFF fitting to CuO reference.  Fine line: experimental data of CuO. Thick line: theoretical fitting.  The inset is the local structure of a Cu atom in the reference model, which shows, around the central Cu atom (plotted with a little bigger size than other Cu atoms), there are two O neighbor atoms located at distance of 1.95Å, two O neighbor atoms at distance of 1.96Å, two O atoms at 2.78Å and four Cu atoms at 2.9Å.  To simplify the fitting, the O atoms at 1.95 and 1.96 Å were treated as one neighbor shell with four O atoms.

Table 8-2  FEFF fitting results on parameters of CuO.  (Note: refer to Table 7-1 for definition)

<table>
<thead>
<tr>
<th>Scattering path</th>
<th>N</th>
<th>R(Å)</th>
<th>dR(Å)</th>
<th>$\sigma^2(10^{-3} \text{ Å}^2)$</th>
<th>$\Delta E_0$(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-O (1nn)</td>
<td>1.8 ± 0.5</td>
<td>1.94 ± 0.02</td>
<td>-0.01</td>
<td>4.2 ± 2.6</td>
<td></td>
</tr>
<tr>
<td>Cu-O (2nn)</td>
<td>0.6 ± 0.2</td>
<td>2.55 ± 0.17</td>
<td>-0.24</td>
<td>1.5 (fixed)</td>
<td>7.4 ± 2.3</td>
</tr>
<tr>
<td>Cu-Cu (3nn)</td>
<td>7.8 ± 2.0</td>
<td>2.93 ± 0.03</td>
<td>0.04</td>
<td>18.4 ± 13.7</td>
<td></td>
</tr>
</tbody>
</table>

Fitting of the EXAFS of this long-period-heated chloride-treated film (Figure 8-8) confirms that the primary peak at 1.53 Å in the phase-uncorrected
radial distribution function, $\chi(R)$, arises from oxygen neighbors with nearest-neighbor distances of 1.95 Å (see in Section 5.2.2.4 for explanation) with a coordination number of 1.5 (Table 8-3) but otherwise consistent with the first nearest-neighbor of CuO (Figure 8-2). The oxygen neighbor at 2.72 Å with

![Graph showing the radial distribution function for Cu K-edge EXAFS of copper diffused CdCl$_2$ treated CdTe film heated in N$_2$ at 200 °C for 4.5 hours. Fine lines: experimental data, thick lines: theoretical fitting.](image)

**Figure 8-8** The $\chi(R)$ functions of Cu K-edge EXAFS of copper diffused CdCl$_2$ treated CdTe film heated in N$_2$ at 200 °C for 4.5 hours. Fine lines: experimental data, thick lines: theoretical fitting.

**Table 8-3** FEFF fitting results on parameters of local structure surrounding Cu atoms in CdCl$_2$ treated CdTe film following long diffusion. (Note: refer to Table 7-1 for definition)

<table>
<thead>
<tr>
<th>Scattering path</th>
<th>N</th>
<th>R (Å)</th>
<th>dR(Å)</th>
<th>$\sigma^2$($10^{-3}$ Å$^2$)</th>
<th>$\Delta E_o$(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-O (1nn of CuO)</td>
<td>1.5 ± 0.4</td>
<td>1.95 ± 0.04</td>
<td>0.00</td>
<td>4.2 (fixed)</td>
<td></td>
</tr>
<tr>
<td>Cu-O (2nn of CuO)</td>
<td>1.7 ± 0.4</td>
<td>2.72 ± 0.10</td>
<td>-0.06</td>
<td>1.5 (fixed)</td>
<td></td>
</tr>
<tr>
<td>Cu-Cu (2nn of Cu$_2$Te)</td>
<td>1.0 ± 0.2</td>
<td>2.54 ± 0.06</td>
<td>0.10</td>
<td>4.3 (fixed)</td>
<td></td>
</tr>
<tr>
<td>Cu-Te (3nn of Cu$_2$Te)</td>
<td>0.7 ± 0.2</td>
<td>2.69 ± 0.29</td>
<td>0.03</td>
<td>22.5 (fixed)</td>
<td></td>
</tr>
</tbody>
</table>
coordination number of 1.7 also contributes to the 1.53 Å peak in $\chi(R)$. But this shell only contributes a small part to the $\chi(R)$ function and has strong interference with other two neighbor shells – copper and tellurium (Table 8-3). We do not observe the second major peak arising from the third-nearest-neighbor of copper atoms at a distance 2.9 Å in $\chi(R)$ as would be expected in CuO.\textsuperscript{122} This demonstrates again that no CuO microclusters formed in this heating-stressed CdTe film, but rather CuO in approximate monolayer form.

It should be pointed out that the transformation of Cu$_2$O to CuO does not require the presence of additional oxygen. The Cu$_2$O may decompose into CuO and elemental Cu under stressed conditions such as annealing. This reaction can be represented as:\textsuperscript{123} Cu$_2$O $\rightarrow$ CuO + Cu. The much larger coordination number (N = 1.0) of the Cu neighbor shell than the one of standard chloride-treated sample (N = 0.2, refer to Table 7-4) may suggest this reaction during the annealing.

The shoulder at around 1.96 Å and the peak at 2.49 Å in the $\chi(R)$ function arise mostly from the copper and tellurium neighbor shells from Cu$_2$Te structure (Table 8-3). The fitting indicates the path lengths of these two shells are identical with the ones of Cu$_2$Te, but with smaller coordination number of the tellurium shell than the one in Cu$_2$Te. This may be understood with the same model as proposed for the chloride-treated film in Section 7.2.2.

8.3 Discussion and Model

As to the interpretation of the Cu$_2$O location proposed in Section 7.3, some of the chloride-treated samples diffused with Cu but without the Au
protective layer were etched with 9% HCl acid for 10 seconds immediately prior to collecting the EXAFS spectrum. The experimental and theoretical (Figure 8-3 and Table 8-1) fitting results indicate that, after etching, most of the Cu$_2$O is dissolved by HCl. This observation indicates that the Cu$_2$O formed in CdCl$_2$-treated films is primarily located either on the back surface or along grain boundaries of the CdTe film (or both) where the HCl can penetrate and dissolve the Cu$_2$O rapidly during the short period immersion. The latest fluorescence studies on the Cu concentration of the peeled off Au layer proves that around 90% Cu is actually located at the back surface mostly in the form of Cu$_2$O and the rest 10% inside the CdTe film. However even with this 10% of the 35Å Cu diffused into CdTe, there are still $\sim 10^{19}$ (cm$^{-3}$) Cu inside the film in average. Given the ionization energy of Cu acceptor in CdTe – 146 meV $^{74}$ and $10^{14}$ (cm$^{-3}$) hole concentration in standard cells, the concentration of electrical active Cu is in the scale of $10^{16}$ (cm$^{-3}$). This suggests even among the diffused Cu atoms which are only 10% of the 35Å Cu layer, most are not electrical active in the CdTe film. The plausible explanation is that they form thin Cu$_2$O and Cu$_2$Te at the CdTe grain boundaries. However there are no available data to investigate the chemical form of this 10% Cu inside the film at the present time. To collect data with good enough quality, four days continuous beamtime for one sample is needed, which is not available for us yet.

Since for CdTe solar cells, chloride treatment is performed before copper evaporation and diffusion, this study suggests that chloride treatment in the typical dry air or He/O$_2$ ambient prepares an oxidizing environment in the polycrystalline
CdTe so that when Cu is diffused in, the O oxidizes the Cu and forms Cu$_2$O mostly at back surface and possibly at grain boundaries also. Cu$_2$O is a p-type semiconducting oxide, and a direct-band-gap semiconductor with $E_g \sim 2.0$ eV. These electronic properties suggest that Cu$_2$O may play an important role as a minority carrier reflector at the back contact and plausibly help to passivate grain boundaries. Interfaces (in our case we focus on the one between CdTe and Au) and grain boundaries typically have large densities of mid-gap states which are effective sites for electron-hole recombination. Depending on the relative electron affinity, the wider-band-gap Cu$_2$O could lead to a conduction-band barrier that inhibits the minority carrier recombination in p-CdTe by repelling electrons at the back contact and the grain boundaries. This can reduce the minority carrier recombination at the back interface and the grain boundaries and benefit the current collection in real cells. Scanning Kelvin probe microscopy$^{124}$ has shown potential barriers at the grain boundaries which we believe are consistent with this interpretation. After heat stress at 200°C in N$_2$, we have found that the Cu$_2$O transforms to CuO which has a 1.34 eV band gap.$^{125}$ The smaller band gap of CuO than CdTe (1.48 eV) suggests that back interface and grain boundaries decorated with CuO may have enhanced electron-hole recombination. Thus, although the Cu$_2$O may inhibit recombination, the long-term annealing leading to transformation of Cu$_2$O to CuO could produce a degradation mechanism in CdTe photovoltaic devices. Detailed studies of band alignment in these materials are clearly needed for confirmation of this mechanism.
Chapter 9 Summary and Conclusion

9.1 Summary

This dissertation has presented results of photoluminescence (PL) of ion implanted single-crystal CdTe and Cu K-edge EXAFS of poly-crystal CdTe thin film.

The first part of this dissertation consisted of the ion implantation designed to obtain uniform impurity distribution from the CdTe surface to a certain depth to match the absorption length of the excitation laser light in PL, and identification of implanted-impurities related luminescence lines through the excitation power dependent and temperature dependent PL studies.

The PL spectral intensities of the Cl-implanted high quality CdTe crystals are found to substantially increase in the overall spectral region compared to spectra of the un-implanted crystal. This indicates decreased nonradiative recombination rate in CdTe after Cl implantation. The Cl-donor-related free-to-bound emission line at 1.553eV and the bound exciton emission line at around 1.590eV are identified through the established power-law function of the laser power in the connection with the free exciton emission at 1.596eV. The activation energy of the Cl donor is also computed to be 53.0meV through the peak energy and fitting to the Arrhenius plot of the Cl-donor-related free-to-bound emission line.
A shallow acceptor state of phosphorus in CdTe is also identified through the PL study of P-implanted CdTe crystals. A P-related free-to bound emission line corresponding to the transition between free electrons in the conduction band to neutral P acceptors is obtained at 1.5355 eV. The ionization energy of neutral P acceptors is identified to be around 70 meV by the peak energy of the free-to-bound line and the temperature dependent intensity of this line. Compared to the ionization energy of the Cu acceptor in a Te site – 146 meV, the shallow P acceptor could be a good candidate for substituting Cu in the future for heavily p-type doping into CdTe cells.

The other part of this dissertation is focused on the local structure of copper in CdTe through an EXAFS study. Both cases of copper diffused CdCl$_2$ treated and non-treated CdTe films were investigated. Copper was found to bind to Te forming Cu$_2$Te in non-treated CdTe film, but to bind to O forming Cu$_2$O in treated film. Evidence was also observed indicating that the Cu$_2$O mostly locates at the back surface of CdTe, probably at the grain boundaries too. Existence of the wider-band-gap Cu$_2$O could lead to a reflecting layer for minority carriers (electrons) in CdTe and to grain-boundary passivation by reducing recombination rates. This could explain why the CdTe films with small grain size, such as magnetron-sputtered films by UT and electrodeposited films by BP Solar, can still generate good cell performance.

The Cu$_2$O in chloride-treated films is also found to be unstable under stressed conditions and can transform into CuO after long period heating of the films such as occurs during normal summer operation of solar cells. This
transformation could reduce grain-boundary passivation and lead to cell performance degradation.

9.2 Directions of Further Studies

I have shown in the previous chapters of the work that PL can be used to obtain important information on impurities in semiconductor materials. The interpretation of the PL results can be complicated by factors such as line broadening and overlapping. I have developed a line shape fitting program combining the instrumental broadening effect to fit the asymmetric peak of free-to-bound emission lines. However the instrumental broadening effect cannot completely explain the low energy side of the free-to-bound lines. Some other broadening mechanisms may be involved and need more studies.

As to the EXAFS study in this work, one should keep in mind that all of the samples were made of sputtered CdTe films. To demonstrate that these effects are general, it would be necessary to carry out the same work on films deposited with other techniques. The EXAFS of copper in as-deposited sputtered films indicates the formation of Cu$_2$Te and we understand this as the benefit of sputtered CdTe, which does not need intentional formation of Cu$_2$Te by chemical etching. Then it will be necessary to prepare some as-deposited CdTe films followed with the same processes of copper deposition and diffusion (without chemical etching) for EXAFS study to see the difference between sputtering and other techniques. It is also necessary to have some chloride-treated CdTe films deposited with other techniques to confirm the existence of Cu$_2$O.
Band alignment across the interface of CdTe and back contact as well as
grain boundaries of CdTe in functional cells will be of great interest. X-ray
Photoemission Spectroscopy (XPS) and Ultraviolet Photoemission Spectroscopy
(UPS) scans with sub-micron scale resolution should be sufficient to provide the
information we need. The coexistence of band mismatching and Cu$_2$O at back
interface and grain boundaries should be confirmed to prove the model proposed
in chapter 8.

Investigation on the location of Cu in functional cells is also of great
interest. Even though our x-ray fluorescence results suggest that Cu$_2$O may be
located at the grain boundaries of CdTe and most at the interface of CdTe and Au
layers, there is no direct evidence yet. The SIMS measurements$^3$ only provide
distribution in one dimension. However, Electron Energy Loss Spectroscopy
(EELS) and Energy Dispersion Spectroscopy (EDS) in association with High
Resolution Transmission Electron Microscopy (HRTEM) or Scanning TEM (STEM)
should be able to reveal the distribution of Cu on a nanometerscale.

The role of Cu$_2$O at the interface of CdTe and Au is also an important
issue relating to the back contact of functional cells. A “re-contact” process, in
which the Au contact is peeled off by epoxy, taking away most of Cu at interface,
and then evaporating a new Au layer, can be employed to prepare cells for
temperature dependent current-voltage (I-V-T) study. Comparing I-V-Ts of fresh
cells, stressed cells, and re-contacted cells will help to reveal the role of Cu$_2$O at
the interface.
Appendix A  Open Circuit Dependence of Dopant Energy Level

A relationship between $V_{oc}$ and quasi-Fermi level of holes in the p-side of a diode solar cell is derived below. All of the equations are referred to Dr. S. M. Sze’s book.$^{126}$

In Sze’s book, the open circuit voltage of a semiconductor diode under illumination is given by

$$V_{oc} = \frac{kT}{q} \ln \left( \frac{J_L}{J_s} + 1 \right) \approx \frac{kT}{q} \ln \left( \frac{J_L}{J_s^0} \right)$$

where the source $J_L$ results from the excitation of excess carriers by solar radiation; $J_s$ is the diode saturation current.

Also

$$J_s = \frac{q D_p p_{no}}{L_p} + \frac{q D_n n_{po}}{L_n} = \frac{q}{\sqrt{\tau_p}} \sqrt{D_p} p_{no} + \frac{q}{\sqrt{\tau_n}} \sqrt{D_n} n_{po}$$

where $D_p$ and $D_n$ are the carrier diffusion coefficient ($D_p$ for holes and $D_n$ for electrons), which are approximately independent of the carrier concentrations for non-degenerated semiconductors and can be treated as constant in our case; $p_{no}$ and $n_{po}$ are the minority carrier concentration of the p-side and n-side, respectively; $L_p$ and $L_n$ are the depletion widths of the p-side and n-side, respectively; $\tau_p$ and $\tau_n$ are the majority carrier lifetimes - holes on p-side and electrons on n-side, respectively.

In our case, we are interested in a CdS/CdTe diode with different acceptor dopants in CdTe (p-side). Let us assume that $\tau_p$ is independent of the
type of acceptor. Since the n-side is kept unchanged, \( p_{no} \) is constant. \( J_s \) only depends on \( n_{po} \).

Since

\[ n_{po} p_p = n_i^2, \]

\[ p_p = n_i \exp \left( \frac{E_i - E_p}{kT} \right), \]

where \( n_i \) is the intrinsic carrier density; \( E_i \) and \( E_p \) are the intrinsic Fermi energy level and the quasi-Fermi energy level for holes, respectively.

Also

\[ n_{po} = n_i \exp \left( - \frac{E_i - E_p}{kT} \right), \]

(3)

When a shallower acceptor is doped in p-side, the \( E_p \) is closer to the valence band and the difference \( - (E_i - E_p) \) is larger (\( E_i \) which generally lies close to the middle of the bandgap). In this case, \( J_s \) decreases as well as \( n_{po} \), according to Equation (2), and \( V_{oc} \) is then larger according to Equation (1).
Appendix B    Computation of Diffused Copper Concentration in CdTe Film

Given a 40Å Cu layer deposited onto the surface of a 2µm CdTe film and assuming all of the Cu is diffused into the film, the copper concentration can be computed as:

\[
\frac{A \times 40 \times 10^{-8} \text{ (cm)} \times 8.96 \text{ (g/cm}^3) \times 6.02 \times 10^{23} \text{ (mol)} -1}{63.546 \text{ (g/mol)} \times [A \times 2 \times 10^{-4} \text{ (cm)}] -1} \equiv 1.7 \times 10^{20} \text{ (cm}^{-3})
\]

where A is a nominal area of the Cu layer; 8.96 (g/cm\(^3\)) is the mass density of solid copper; 6.02 x 10\(^{23}\) (mol\(^{-1}\)) is the Avogadro constant; 63.546 (g/mol) is the molar mass of copper.
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