The Realization of a New Band Gap Engineered Photoferroelectric Photovoltaic Device with High Photocurrent

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By

Steven Bennett

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ABSTRACT

In solar photovoltaics the conversion of light energy into electrical energy involves two fundamental steps. The first is the effective generation of charge carriers and the second is the presence of an electric field gradient to carry that charge and create a photocurrent. Traditional semiconductor photovoltaics utilize the electric field from a p-n junction to separate the light-generated charge carriers from their counter-part holes. However, the low electric fields present in these devices result in charge carrier loss due to electron-hole recombination. By increasing this electric field we can decrease the probability of electron-hole recombination; essentially increasing the effective photocurrent. This is where the promise of the ferroelectric photovoltaic effect lies (photoferroelectrics). Currently, the state of the art in photoferroelectrics shows that a high open circuit photovoltage is achievable through the use of epitaxial bismuth ferrite (BFO) thin films. However, its bandgap is comparatively large (2.35eV) giving it a low optical absorption efficiency, and therefore a low photocurrent.

This proof of concept demonstrates a novel approach towards enhancing the photocurrent from photoferroelectric BFO. The idea is to incorporate a bandgap engineered, discontinuous nano-granular thin film ferrite, (Cd$_x$Mn$_{1-x}$Fe$_2$O$_4$ [CMFO]), with BFO in a heteroepitaxial structure. The result is a photovoltaic device that has a spontaneous electric polarization and high photocurrent without the need for a p-n junction. An order of magnitude increase and record photocurrent was measured by incorporation of this discontinuous CMFO layer. The giant photocurrent enhancement can be explained by the overall increase in photo-induced charge carriers originating from the added narrow bandgap CMFO. Furthermore, the magnetic characteristics of both layers could lend to the possibility of tuning the absorption of the device by use of an external applied magnetic field.
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INTRODUCTION

Radiation from the sun amounts to approximately 10,000 times the energy utilized by humans worldwide (1,2). The sun’s energy is what drives all natural processes occurring on the planet and so it’s no surprise that we seek to harness its power to fuel our technologies. Photovoltaics are our primary harvesting method for converting solar energy to electrical energy. There is now more than 100 GW of solar power generators installed worldwide, and more than 80% of those contain silicon p-n junction-based modules. Thanks to decades of crystalline silicon being refined for the computing industry, silicon has become the cheapest and most abundant semiconductor material. This, and its favorable bandgap for visible absorption, has made silicon the perfect material to foster the growth and continued development of the photovoltaics’ industry. But the future of photoconversion does not necessarily lie with silicon-based p-n junction technology. Research into other technologies has seen a rise in solar cell efficiencies based on other semiconductor materials such as GaAs and CdTe. Also being researched are quantum dot cells, dye sensitized cells, organics, perovskite cells and various types of thin film heterostructure technologies. In this thesis we present a new type of solar technology that can be thrown into the mix of competing technologies to silicon. Fabricated here was a new type of ferrite-based photoferroelectric device that demonstrates a high photocurrent density comparable to other leading photovoltaic technologies.
BACKGROUND

In the traditional silicon p-n junction incoming radiation is transferred to electrical energy by exciting a valence electron across the bandgap to the conduction band where it contributes to the photocurrent. Essentially, the incoming radiation generates photo-induced charge carriers. The carriers consist of electrons accompanied by their constituent holes which they leave behind at their original, lower energy state. In order to prevent the electrons from losing energy and falling back to their original energy state (combining with their hole) there needs to be a constant separation between these two energies. This is achieved by an electric field, also called a voltage or potential. In the p-n junction a region of the solid known as the depletion region creates this potential that serves to keep the electrons from recombining with their holes (Figure 1). This region can also be seen as an area where a force is applied to the electrons, increasing their momentum, and carrying them towards the electrode, and away from the holes which drift towards the opposite electrode (cathode). The region is created by doping the surface of p-type silicon with atoms that poses a high n-type carrier concentration. In doing so there is region located at the interface of the doped n-type area and the undoped p-type area where the electrons and holes recombine creating an area that is essentially void of any carriers (i.e. the depletion region). Since the area on either side of the depletion region has oppositely charged carriers separated in space there is a charge gradient, a.k.a. an electric field. Without this depletion region the photo-induced carrier generation rate would be largely balanced by the electron-hole recombination rate resulting in little to no photocurrent generation. A photoferroelectric serves to eliminate the need for this depletion region because it has its own intrinsic spontaneous electric field. This will be discussed in greater detail later in this thesis.
Ferroelectrics

Functional oxides have been in development for decades and recently those having multiferroic properties have risen to the forefront of materials research. BFO (i.e., BiFeO$_3$) is a ternary oxide with a perovskite structure. Like other ternary perovskite oxides BFO has a chemical formula (ABO$_3$) and is made up of corner sharing octahedra with A-cations (Bi) coordinated by twelve oxygen ions, and B-cations (Fe) by six.

Unique to the complex oxides is the wide range of electronic/magnetic properties that can be achieved by changing the concentration of the anion, (or substitutional elements for the anion as in cadmium manganese ferrite (CMFO)). CMFO is possible because of another important characteristic of the complex oxides where the structure can easily accommodate a wide range of valence states on both the A and B lattice sites (i.e. A$^{+1}$B$^{+5}$O$_3$, A$^{+2}$B$^{+4}$O$_3$ and A$^{+3}$B$^{+3}$O$_3$ in the...
perovskites) (20). This gives a lot of flexibility when doping the structure substitutionally to tune various materials characteristics.

There are 32 classes of crystals in materials science. Eleven of those possess symmetry centers. Of the 21 that don’t, 20 are piezoelectric. The piezoelectrics produce an electrical polarity (a.k.a. an internal electric field) when exposed to a mechanical stress (3). Of these 20 piezoelectric crystal structures, 10 have an internal spontaneous polarization even without application of mechanical stress. The electrostatic field present in these crystals cannot be measured directly however, because under normal circumstances free charges, either from within the crystal itself or from the outside environment, accumulate on the surface. This charge accumulation effectively screens, or compensates, the electric field due to the internal polarization. In order to measure the internal electric field an external perturbation of the screening charges can be used. The most fundamental method for doing this is to vary temperature. By changing the temperature charges will build up by influence of the internal polarization, creating a measurable voltage potential. This material effect is called pyroelectricity; hence why this class of materials is often referred to as the pyroelectrics.

Any dielectric material will develop an electrostatic polarization when an electric field is applied to it. Effectively, the added electric field aligns the poles of the polar molecules in the system creating an electrostatic buildup in the crystal. But the 10 polar crystal classes (pyroelectrics) possess a spontaneous polarization, or displacement, of these bipolar molecules within the lattice. In some of these materials a strong enough electric field can switch the polarity of this polarization. These materials are called the ferroelectrics.

The ferroelectrics were named after their characteristic resemblance to the ferromagnetic materials that had already been discovered. Where this resemblance shows up is in the P - V
(potential versus voltage) loop of such a material. When a material is subjected to a P - V measurement voltage is applied to the sample and its polarization is measured. The trend for such a loop would reveal a straight line for most dielectric materials. However, when a ferroelectric is tested in this manner a hysteresis in polarization will be evident, much like the hysteresis shown by a ferromagnetic material in taking a M - H (moment versus applied field) (see Figure 2).

**Ferroelectric Hysteresis**  **Ferromagnetic Hysteresis**

![Ferroelectric Hysteresis](https://www.pubs.rsc.org)

![Ferromagnetic Hysteresis](https://www.pubs.rsc.org)

**Figure 2: Visual comparison between ferroelectric hysteresis loop and ferromagnetic hysteresis loop**

The big difference to note between a ferroelectric and a ferromagnetic is that the spontaneous field in a permanent magnet (ferromagnet) can always be measured, while that for a ferroelectric will be compensated for by screening charges. This is why there isn’t a bar magnet equivalent for a ferroelectric material.
Bismuth Ferrite (BiFeO$_3$)

In the past 10 years attention in ferroelectric materials research has turned to those which are lead-free, have strong intrinsic polarizations and high ordering temperatures. A prime example of this new generation of ferroelectrics is BFO (BiFeO$_3$). This thesis focuses on the use of epitaxial BFO grown on STO (100) substrates for its preferable ferroelectric, magnetic and semiconducting properties when grown on such a substrate (see section titled Bismuth Ferrite (BFO) for more on this). Not only do its photoferroelectric properties make it useful in the device demonstrated here, but its magnetic properties might prove to make such a devices optical absorption tunable in future studies.

Multiferroic BFO thin films have proven to have very high polarization fields (4). Furthermore, growth of epitaxial BFO on STO results in polarization domain wall formation in-plane with the substrate. These poling domains are a consequence of the minimization of elastic and electrostatic energy in the film. In recent years a number of studies have shown how the orientations and directions along crystal planes can be precisely controlled by changing substrate materials and crystallographic orientations (5,6,7).

The biggest take back from studies which probe the formation of domain walls is the interplay between electrostatic and elastic straining mechanisms in epitaxial films. This is to say that the formation of domain walls is dominated by two competing factors that depend on both the electronic and crystal structure of the film and how it interacts with the underlying crystal lattice of the substrate material. For instance, when growing on a conducting complex oxide (RuO) bottom electrode the carriers in the layer will serve to locally (and in the thinnest film cases completely) depolarize the film. How this works is that the RuO’s free electrons flow into
the ferroelectric BFO, providing more charge to screen the internal electric field, and in turn decreasing the crystals electrostatic influence on domain formation. This will in turn leave the most dominant domain scaling mechanism to be that of elastic strain with the substrate (such as a lattice mismatch). Alternatively, when the film is grown on an insulating STO substrate the electrostatic forces play a much larger role in the domain formation (6) (Figure 5).

To fully understand the high polarization fields measured in thin film bismuth ferrite it would help to review the recent findings made by S. Y. Yang et. al. in 2010 (8). In that study the authors measured above bandgap voltages in epitaxial bismuth ferrite (BFO) grown on dysprosium scandium oxide (DSO) 110 substrates. They further investigated the phenomenon by mapping the domain structure of the films by piezoelectric force microscopy (PFM) and found the striped domain pattern shown in Figure 3.

![Figure 3: PFM images of BFO's striped domain wall pattern when grown on DSO 110 substrates /S. Y. Yang et. Al. 2010/](image)

Their hypothesis was that the electrostatic ferroelectric domains in the structure were serving to increase the open circuit photovoltage from the film. To test their hypothesis, planar
electrodes were patterned on the surface of the films both perpendicular and parallel to the striped domain walls (Figure 4(a) & (b)). They found that with the electrodes patterned perpendicular to the domain walls little to no photocurrent was measured, while the samples with electrodes patterned parallel showed a measurable photocurrent (Figure 4(c) & (d)). This establishes clear proof that the domain walls are contributing largely to the above bandgap voltages in these BFO films. This proof led the authors to define this domain wall driven photoferroelectric effect in thin films as being driven by an entirely a different mechanism than that for the bulk.

Figure 4: Planar electrodes patterned both parallel (a) and perpendicular (b) to electrostatic domain walls. Graphs (c) and (d) shows light on (red) and light off IV curves for both orientations (graph (c) is for orientation (a) and graph (d) is for orientation (b). Circled on graph (c) is the zero biased photocurrent density of the device of $-10^{-4}$ A/cm$^2$. 
In another study by C. Himcinschi et al. in 2010 (9) BFO 001 films were grown on strontium titanate (STO) 001 which is a more cost effective substrate material than DSO. They, too, found a clear electrostatic domain pattern in their films with PFM (Figure 5).

![Figure 5: PFM image of electrostatic domains in epitaxial BFO 001 thin films grown on a Nb:STO 001 substrate [C. Himcinschi et. Al. 2010]](image)

This domain pattern may not be the striped structure found in the films grown on DSO, but it does provide a domain wall structure that can be poled by an external field and has been shown to hold a strong internal electrostatic field suitable for the proof of concept to be fabricated in this thesis (10). The feasibility of a device made with STO rather than the more expensive DSO was also taken into consideration as a strong motivation towards using it as the preferable substrate of choice.
Photoferroelectrics

Figure 6: Simplified schematics for (a) The interfacial PV effect in a semiconductor p-n junction and (b) The bulk photovoltaic (PV) effect in a ferroelectric thin film.

BFO's other interesting characteristic is its optical properties as a photovoltaic. Materials that show both a bandgap near or close to the visible and ferroelectric properties are called Photoferroelectrics. The term photoferroelectric was coined quite a while ago and their discovery is not new to science (11). Research into such materials has been limited, but recently there has been a resurgence of their study in the field. Although the semiconductor characteristics of the ferroelectrics have been known for 50 years their low power conversion efficiency has deemed them unsuitable for photovoltaic technologies. The recent finding of above bandgap photovoltages outlined in the previous section by S. Y. Yang et. Al. in 2010 has sent ripples across the ferrite and multiferroics research community, spurring new interest in the photoferroelectrics, and specifically BFO thin films.
The excitement in the use of a photoferroelectric in photovoltaics applications spawns from their spontaneous electric field. The traditional semiconducting photocell uses the electric field induced by the n-type doping of p-type silicon. At the interface of the doped region and the non-doped region lies a depletion region where there lies no charge. This region effectively creates an electric field which serves to separate the photo-excited charge carriers from their constituent holes in the semiconductor. Without the electric field the excited charge carriers will fall back to their unexcited state (recombine with its hole) at a rate comparable to that which they are generated (effectively canceling each other out and not inducing a current). This is the basic functioning of the p-n junction photodiode, but the design is not ideal. The p-n junction has a $V_{oc}$ (open circuit voltage, aka electric field) which is low and less than satisfactory for charge separation. By failing to offset the recombination rate it winds up detracting from the overall efficiency of the system. In theory, by increasing the electric field one can decrease the electron hole recombination rate, effectively increasing the photocurrent and efficiency of the device. This is the promise of a photoferroelectric.

Not only does a photoferroelectric material have a large electric field but it does so without the need for a p-n junction (Figure 6). Photoferroelectric BFO has been shown to have a higher $V_{oc}$ than a typical p-n junction (8). In fact the effective electric field in most ferroelectric materials is approximately an order of magnitude higher than in a p-n junction. The problem facing implementation of BFO in a solar harvesting device is its large bandgap (2.67eV, ~465nm) (12). This large bandgap has the resulting effect of a low optical absorption and, therefore, low photocarrier generation. The present work has been to combine a narrow bandgap ferrite semiconductor with epitaxial BFO to create a thin film device with a spontaneous electric polarization and high photocurrent.
DEVICE THEORY

The device fabricated here harnesses the internal electric polarization of BFO thin films grown on STO (001) substrates. Growth on these substrates has proven to show a domain pattern that will contribute to the functioning of the device by enhancing the photoferroelectric effect and produce above bandgap $V_{oc}$ (8,13,14). It was also shown that lateral electrodes across domain walls will produce high voltages and an enhanced photovoltaic effect. Though most of this work was concentrated on the switchable photovoltaic effect for applications in sensors and memory, separately BFO has been considered for its photoferroelectric effect as well (15,16) but due to its low bandgap (2.67eV) it produced only small photocurrents (~0.4nA). The idea here is to use BFO for its high ferroelectric polarization but enhance the photocurrent by depositing a discontinuous nanocrystalline layer of narrow bandgap cadmium manganese ferrite (CMFO). CMFO is a good match for this application because it too is a perovskite oxide, and theory has shown that its bandgap should be well within the visible (17) at 1.36-1.39eV.

Figure 7: Cross sectional diagram of device structure/operation.
Figure 7 shows a cross sectional image of the CMFO + BFO photovoltaic device. Sunlight induced charge excitations come from both the epitaxial BFO film and the discontinuous nanocrystalline CMFO (with the majority coming from the narrow bandgap CMFO). After generation the charges migrate via BFO’s internal electric field. The charges generated from the CMFO and BFO are then collected at the surface electrodes that come directly in contact with the BFO. The key feature of the design is the interdigital planar electrodes (also shown in Figure 39) which both allow for light to radiate the underlying ferrite layers and while still making electrical contact with both the CMFO and the BFO to capture the photocurrent.
MATERIALS SYNTHESIS & CHARACTERIZATION

Devices were fabricated by in-situ PLD thin film growth followed by photolithographic patterning of inter-digital Ti/Au top electrodes. This process, along with the methods for thin film synthesis and characterization are outlined in this section.

Cadmium manganese Ferrite (CMFO)

Overall there is very little work done on the material characteristics of CMFO. Up until this thesis work on the thin film or nanostructured form of CMFO has yet to be published. However there were a few studies that delved into the bulk magnetic, thermoelectric and charge transport studies of the system. In 2011 an *Ab initio* study was done to probe the theoretical properties of a $\text{Cd}_x\text{Mn}_{(1-x)}\text{Fe}_2\text{O}_4$ system. Their findings put the bandgap of the material in the optical regime (18). For a composition of $x = 0.25$ they calculated a bandgap of $1.3962\text{eV}$. They found that as the Mn composition increased the bandgap decreased (Figure 8).

![Cd$_{(1-x)}$Mn$_x$Fe$_2$O$_4$ Bandgap](image)

Figure 8: Theoretical bandgap of CMFO from *ab initio* studies (18). Red line indicates concentration chosen for study in photovoltaic device.
Though increasing the Mn concentration is a route to a narrow bandgap it also alters the magnetic coercivity ($H_c$), saturation magnetization and phase fraction of Cd(Mn, Fe)$_2$O$_4$ in the system. This was found in a study by Bing W. Jong from the Georgia Institute of Technology and P. Darell Ownby at the University of Missouri-Rolla. In their work they synthesized bulk samples of the material by powder ball-milling then performed a subsequent calcination with varying cadmium concentrations (19). They found that at cadmium concentrations lower than around $x = 0.2$ (higher than $x = 0.8$ for Mn concentration) the phase % of Cd(Mn, Fe)$_2$O$_4$ falls off dramatically. This indicates that at these concentrations the constituent species are immiscible (a miscibility gap) (Figure 10). They also plotted the saturation magnetization which is at a peak for the largest concentrations of Mn and falls off to a very low value for $x = 0.5$ (Figure 8). Their findings also show that a peak in the coercive field is seen at $x = 0.3$ (Mn concentration = 0.7).

For the initial purposes of this proof of concept study it was especially important to retain a large magnetic moment and decent coercivity in the system to test whether application of a magnetic field could further tune the absorbance of the CMFO. In the device this absorption tuning could lead to a more specified photovoltaic response by increasing the photocarrier charge generation for any specific radiation wavelength regime. It is for these reasons that for the device a concentration for Cd$_x$Mn$_{(1-x)}$Fe$_2$O$_4$ of $x = .3$ was chosen. Based on these previous studies and their findings mentioned above this concentration was the best starting point to realize good magnetic characteristics and a bandgap in the visible.
Figure 9: Br/Bm and coercive field strength at a drive of 50e and a 1kHz vs. cadmium concentration, (x), for Cd$_{x}$Mn$_{(1-x)}$Fe$_2$O$_4$ (19). Red line indicates concentration chosen for study in photovoltaic device.

Figure 10: Room-temperature saturation magnetization vs. cadmium concentration, x, for Cd$_{x}$Mn$_{(1-x)}$Fe$_2$O$_4$ and percent conversion to Cd(Mn, Fe)$_2$O$_4$ vs. cadmium concentration, x, for the composition xCdO + (1-x)MnCo$_3$ + $\alpha$=Fe$_2$O$_3$ reacted at 900°C for 2 hours. Red line indicates concentration chosen for study in photovoltaic device.

It’s important to note that these studies are for bulk CMFO and might not correlate to the best concentration to gain these properties for the thin film. More work into understanding how concentrations of Mn and Cd effect the properties of the thin film should be done in the future.
CMFO Thin Film Growth

The first step in this proof of concept was to synthesize CMFO as a thin film and measure its optical bandgap. If it was determined that the optical bandgap agrees with theory than the next step is to vary growth conditions to try to attain a discontinuous nanoparticle morphology for use in the final device. Growth of CMFO films was attempted via both Magnetron Sputter and Pulsed Laser Deposition (PLD).

Magnetron Sputter

Initial attempts at growth of CMFO were done by Magnetron Sputter. Magnetron Sputter is a thin film growth technique. Unlike evaporation growth techniques, sputter can deposit films of insulating materials like ceramics and oxides as well as metals. However it is unable to deposit magnetic materials. Its operation relies on a low pressure medium of a working gas. This working gas can be an inert gas such as Argon, a reacting gas such as Oxygen, or a mixture of the two. In the chamber this working gas is ionized by a large electric bias put on the anode. For an insulating target material an RF bias is used and for a conducting target a DC bias may be used. Embedded in the anode is an array of permanent magnets that serve to concentrate the charged ionic plasma over the target. The target, which is resting on the anode, has a concentration of ion concentrated over it in the magnetic field from the underlying permanent magnet array. It is these charged ions that are accelerated towards the sample in the large electric field that is produced by the anode. Collisions with the target eject matter from the target in the form of atoms, atom clusters or molecules. The ejecta has no charge and therefore is
uninfluenced by the electric field produced by the anode and travels in a straight line towards the substrate to form a highly conformal thin film.

![Magnetron sputter diagram](image)

**Figure 11**: Magnetron sputter diagram of Ti/Au electrode deposition. For attempts at deposition of ferrite thin films the titanium target is replaced by the targets shown in Figure 12 and Au foil pieces are removed.

The sputter system that was used for the initial attempts has 3 sputter heads and two power supplies (one RF and one DC). Since CMFO is ferromagnetic creation of a single phase ferrite target for sputter is not possible. The reason why magnetic materials do not work well for magnetron sputter is because the magnetic field that confines the ionic plasma is blocked by the magnetic target material. Due to this it becomes impossible to strike a plasma in the chamber with the anode.
The devised approach would be to embed CdO/MnO pellets in a Fe$_2$O$_3$ target and anneal them together in an oxygen environment. The result was an embedded pellet target as seen in Figure 12.

Figure 12: Embedded pellet ferrite target and their annealing temperatures and times.

With this method tuning elemental concentrations in the film relied on the creation of a new embedded pellet target with different numbers and diameters of CdO pellets, which proved to be arduous and time consuming. Also, difficulties arose when the size and shape of the target were affected by the relative shrinkage of both the CdO pellets and the Fe$_2$O$_3$ disk. Many targets cracked either during sintering or during sputtering when heated. After breaking damage to the sputter head started to occur and sputtering of the copper anode and neodymium based magnets served to ruin the depositions. Due to these numerous difficulties sputter was decidedly not the best approach.
Pulsed laser deposition (PLD)

Unlike magnetron sputter, pulsed laser deposition allows for the use of both magnetic and nonmagnetic materials. The process for the deposition of a target material is by ablation with a pulsed high intensity KrF laser (Figure 13). A high intensity pulsed laser is directed at a target material in a vacuum chamber filled with a working gas at low pressure. When the high intensity laser radiation penetrates the target material the electric fields created are great enough to strip the penetrated volume of electrons. These free electrons heat up rapidly as they move in the quickly changing electric field. This serves to heat the surrounding matrix to the point of vaporization. This vaporized material is sent towards the substrate in a combined vapor and plasma plume.

The working gas can be either inert, reactive or a combination of both. For ferrites a low pressure (100mTorr) oxygen atmosphere is necessary in order to maintain a stoichiometric film. Using laser ablation rather than sputter allows for the deposition of a film that has relatively the same chemical composition as the target material, but for oxide materials oxygen is lost in the process. Many factors affect the deposition rate and morphology of the final film. Future studies may vary parameters such as laser power/pulse rate, raster speed/pattern, substrate temperature and background gas pressure/composition. But for this study parameters were kept constant for all the samples studied.
One unique characteristic of the PLD chamber used for this study was the method used for substrate heating. Most PVD chambers use a conductive substrate heater. This essentially consists of a heating element embedded in the sample holder. The main transfer of heat to the substrate is by conduction from the filament behind the sample. The deposition chamber that was used in this thesis consists of 6 separate tungsten filament heating bulbs surrounding, but not in contact with, the sample holder (see Figure 13). This allows for rotation of the sample in the deposition region without the need for electromechanical power contacts. This setup results in the sample being primarily heated radiatively rather than by conduction. There is also a small amount of convective heating from the working gas in the chamber but the majority of the
heating is done radiatively. This results in a more uniform substrate temperature gradient as compared to the traditional filament substrate heater, and therefore more uniform samples.

**PLD Growth of CMFO**

PLD growth of CMFO was first done with a pressed powder pellet target with a composition to compensate for the relative deposition rates of the constituent powders. This target was used to grow samples of CMFO on glass slides for optical absorption measurements (Figure 11). The tuning of the target powder concentrations was done by making a target and doing EDAX of a deposited film from that target. The concentration values were tuned by changing the target powder composition.

A series varying sample thicknesses were grown from these pressed targets on standard laboratory glass slides. Pressed powder targets were fabricated by first measuring out the constituent powders to meet a target of $\text{Cd}_x\text{Mn}_{(1-x)}\text{Fe}_2\text{O}_4$, $x = .3$. After weighing the powders were mixed via ball mill for 15minutes in forward, then again in reverse, at 350rpm in reagent alcohol. After mixing via ball mill the powders were dried on a hotplate at 80°C. Then they were axially pressed into a pellet 1.25” in diameter with 4tons of force. After mounting the untreated
powder pellet target into the PLD they were deposited with the deposition conditions outline in Table 1.

**Table 1: Deposition conditions of CMFO film for optical absorption studies**

<table>
<thead>
<tr>
<th>Condition</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser pulse frequency</td>
<td>10Hz</td>
</tr>
<tr>
<td>Substrate temp</td>
<td>500°C</td>
</tr>
<tr>
<td>Base Pressure</td>
<td>1.5-2.5 x 10^{-6} Torr</td>
</tr>
<tr>
<td>Working Gas Pressure</td>
<td>1mTorr (by Baritron Vacuum Guage) [20% Ar, 80% O\textsubscript{2}]</td>
</tr>
<tr>
<td>Deposition time</td>
<td>varied to achieve an array of sample thicknesses (measured by x-ray reflectivity)</td>
</tr>
</tbody>
</table>

It was determined that excessive target erosion of the pressed pellet could start to effect the growth rate and film uniformity from sample to sample. It was determined that a more durable target was needed for the rest of the study and therefore a sintered/calcined CMFO target was created. The make-up of this target could be the same as the target composition. This is because after sintering the target will have a fairly uniform phase composition. The pressed powder target constituted powder grains of the three different constituent powders (CdO, MnCO\textsubscript{3}, Fe\textsubscript{2}O\textsubscript{3}), and each of these vaporize at different rates. But for the uniform phase sintered puck the rate is the same across the sample.

The fabrication of the sintered target was done much the same as that for the pressed pellet with an extra annealing step done in air. The powder was weighed and mixed via ball mill (15min, 350rpm, 1cycle, then reverse) in alcohol, then dried on a hotplate at 80°C. The composition of the powder can be found in Table 2. A low vapor pressure for Cd results in some boil off at elevated temperatures during sintering. To account for this, a concentration of x = .32 was used (.02 higher than the target of x = .3). The dried powder was axially pressed in a 1.25”
diameter die press with 6 tons of force. The compaction force was 2 tons higher than the previous target to try and achieve a higher density compact for calcination. Annealing was done in a box furnace, in air, at 750°C for 4 hrs.

<table>
<thead>
<tr>
<th>POWDER</th>
<th>Ratio</th>
<th>Weight for 30g Batch</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdO</td>
<td>.1473</td>
<td>4.419g</td>
</tr>
<tr>
<td>MnCO₃</td>
<td>.2802</td>
<td>8.406g</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>.5725</td>
<td>17.17g</td>
</tr>
</tbody>
</table>

Table 2: Powder compositional make-up for CdₓMn₁₋ₓFe₂O₄, x = .32 target for calcination
**CMFO Film Characterization**

CMFO films were grown and characterized by VSM, XRD, XRR, EDAX, SEM and UV-Vis absorption. The results of all these experiments, presented within this section, agree closely with past literature and theory.

**Magnetic Measurements of CMFO Films**

Magnetic characterization was carried out by vibrating sample magnetometry (VSM) using a Lakeshore 7400 series magnetometer capable of reaching 1.25 Tesla of applied field. This system is a traditional Foner style magnetometer (Figure 15) after its inventor Simon Foner who, in 1955 at MIT’s Lincoln Labs, was the first to measure the magnetization of a material using this setup. How it works is by vibrating the sample sinusoidaly in a uniform magnetic field. Nearby, also in the magnetic field but stationary, are pickup coils. As the sample moves through the field a proportional sinusoidal induced voltage is induced in the pickup coils which are stationary in the field. The voltage is directly proportional to the samples’ magnetic moment. In the Lakeshore system, to minimize noise, a lock-in amplifier is used to measure this voltage. The lock-in uses a reference voltage from the piezoelectric vibrator located in the vibrator head.
The magnetic characteristics of a material are described by a combination of electronic and mechanical fundamentals. The strength of the electromagnetic interactions that the material has (its magnetization) are defined by the material's magnetic moment. The term moment correlates directly with the well-known physical principle used in mechanics. It’s basically the torque experience by the material when it is in the presence of a magnetic field, (also known as the “moment” in mechanics).
To explain this further we look at the basic example of a current loop in a magnetic field (B) (see Figure 16). You can replace this current loop with a magnetic material which has a spontaneous magnetic field not unlike that which is created by the current traveling though the wire. Refer to the top view and notice the orientation of the loop parallel to the field lines. In this orientation the net mechanical torque on the wire will be,

$$\tau = IAB.$$

Where A is the area of the loop and I is the current through the loop. If you look at the top view at an angle ($\theta$) in the figure than you will notice that the value for the torque changes to,

$$\tau = IAB(\sin(\theta)).$$

To simplify the orientation dependence of the torque we can define a new vector quantity, $\mu^\rightarrow$, or the magnetic dipole moment,

$$\mu^\rightarrow = NIA^\rightarrow.$$

The direction of the vector is determined by the right hand rule so the final expression for the torque is,

$$\tau^\rightarrow = \mu^\rightarrow \times B.$$

This magnetic dipole moment is the main parameter used when considering the magnetic properties of magnetic materials. How the magnetic dipole moment responds to the applied magnetic fields strength and direction (orientation) can tell us about how the spins align in the material and how they interact with each other in the crystal. The most important of these properties are the remanance ($M_r$), the saturation magnetization ($M_s$) and the coercivity ($H_c$) (see Figure 17).
The $M_r$ is a measure of the magnitude of magnetic dipole moment that the sample still experiences after the applied field is reduced to zero. Materials that are ferromagnetic have a spontaneous magnetic field. This means that even when the material does not have an applied magnetic field its electron spins are aligned by an inherent magnetic anisotropy. The strength of this spontaneous internal field is essentially the $M_r$. The presence of a large $M_r$ is why ferromagnetic materials are also called permanent magnets.

The $M_s$ is the maximum magnetic moment that the sample has at saturation. Saturation occurs when all the electron spins are aligned with the applied magnetic field. Essentially the electron spins align with the field when it is applied but the spontaneous field in the material works against their total alignment, pulling the vector in the other direction. The point at which the spins alignment with the spontaneous internal field is overcome by the external applied field is $H_c$, or the coercive field occurring once the magnetic moment falls to zero.
How we determine these parameters is by ramping the applied external magnetic field, H, from negative to positive, and then back again. The result is a graph of the magnetic moment picked up by the pickup coils, M (in emu), versus the applied magnetic field, H (in Oe).

![CMFO Magnetization Curves](image)

*Figure 18: Magnetization curves of various thicknesses of CMFO thin films grown on glass slides. Data was obtained by VSM.*

VSM measurements for a series of thicknesses of CMFO thin films are shown in Figure 18. From these you will notice that the saturation magnetization increases with thickness/deposition time. The thicknesses of the films were calculated based on deposition rates measured by x-ray reflectivity (*see section on XRD/XRR*). Since there is the presence of a magnetic remanence at zero field (\(M_r\)) the material is shown to be magnetic. This agrees with previous studies that also measured the magnetic characteristics (19). Technically the materials
moment is a result of super-exchange interactions between manganese atoms, (mediated by the oxygen anions in the lattice). The spin orientation has been classified to be ferrimagnetic.

The $M_s$ of the films was plotted as a function of film thickness in Figure 19. It shows a roughly linear dependence of the moment as a function of thickness. This makes sense because with more material deposited the moment should increase. It also helps to verify the accuracy of thickness measurements made by x-ray reflectivity (XRR).

Figure 19: Magnetic moment as a function of film thickness for a series of CMFO samples grown on glass slides. BLUE = Samples whose thicknesses were measured directly by XRR. RED = Samples whose thickness was calculated based on a relative deposition rate of .24 nm/min.

The $M_s$ of a material tends to be very closely related to composition and the number of bohr magnetons per atom of the structure. The $H_c$, on the other hand, depends largely on many other factors. A few examples of such factors are crystallinity, defect concentration and morphology. A plot of the $H_c$ versus the thickness is shown in Figure 20. It was found that for these samples the $H_c$ does not change much with thickness until sample thickness falls below
~3.5nm. This trend is explained by known 1d confinement effects for ultra-thin magnetic films. These effects are largely encompassed by spin canting at the interface. The effect increases with decreasing sample thickness below a lower limit (in this case its ~3.5nm).

![Hc vs. Thickness](image)

**Figure 20**: The coercivity as a function of sample thickness for CMFO samples grown on glass.

Another study of the magnetization of CMFO grown on 4 other substrates was demonstrated as well. In this PLD growth of CMFO from a sintered ferrite target was done for 20min at 900°C, 1mTorr (20%Ar and 80%O₂). On the substrate holder was mounted Si (111), STO (110), STO (100) and SiO₂ (0001). Figure 21 shows the room temperature magnetization hysteresis loops from each of the samples.
These loops possess a higher coercivity, higher squareness and higher saturation magnetization than those grown on glass slides. This higher squareness indicates a larger anisotropy present in the system and could have occurred because of a few factors. Firstly, since these substrates can withstand temperature much higher than the glass slides used thus far, the films were grown at an elevated substrate temperature, (900°C as opposed to 500°C). This higher temperature induces a higher atomic mobility during growth, which leads to a higher crystallization rate. For these films the degree of crystallinity is directly proportional to the magnetocrystalline anisotropy. Also adding to the squareness is the crystallographic orientation of the film with the substrate, which seems to have been best oriented on the STO 001. This is a very positive result because in the device BFO and CMFO are to be grown on STO (100) and, as
seen here, the CMFO film on STO (100) showed the highest saturation magnetization and largest apparent squareness (box-like hysteresis).

These solid magnetic properties measured in CMFO also point to the possibility of tuning the absorption response of the films by an external magnetic field. In a device such as this, magnetostrictive strain in the system could serve to change the effective bandgap of CMFO. It would be even more apparent if the CMFO were fabricated as isolated nanoparticles under 3 dimensions of quantum confinement (quantum dots). This would make for a tunable multiferroic photovoltaic that can be used in a wide array of sensor applications.

Morphological, Compositional and Crystallographic Characterization of CMFO Films

Compositional concentrations of the thin films were determined by energy dispersive x-ray analysis (EDS or EDXS) which was done in-situ with scanning electron microscopy (SEM). Energy dispersive x-ray spectroscopy works by bombarding the surface of a sample with high energy charged particles (in this case electrons from the SEM’s electron gun). The high energy electrons transfer their energy to those electrons that orbit the atoms in the system. This excites the electrons and raises them to a new energy shell leaving behind a hole. This hole gets filled by an electron from an outer shell, which has to lose energy to fill the hole. Some of this energy is emitted as x-rays; the larger the difference between the energy of the hole and the energy of the electron the higher the energy of the x-ray. Using a scintillation detector this radiation is collected and transferred to a histogram of energies. Since all atoms possess a unique excitation signature (because no two atoms’ valence structure is alike) the energies in the histogram can be directly correlated to the relative elemental concentrations in the material.
One note to make on EDS is that it’s accuracy depends on the amount of material that is excited by the electron beam. With ultra-thin films such as the ones used here, most of the signal in the EDS spectrum is from the underlying substrate (in this case the STO 110). This lends a larger than normal degree of error to the EDS results and therefore these results are used merely for benchmark purposes to verify that we are in the correct concentration regime within a few percent error.

**EDAX of CMFO:**

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Fe</th>
<th>Mn</th>
<th>Cd</th>
</tr>
</thead>
<tbody>
<tr>
<td>STO (100)</td>
<td>65.96</td>
<td>24.44</td>
<td>9.61</td>
</tr>
<tr>
<td>STO (110)</td>
<td>67.02</td>
<td>23.52</td>
<td>9.95</td>
</tr>
<tr>
<td>IDEAL</td>
<td>66</td>
<td>23</td>
<td>10</td>
</tr>
</tbody>
</table>

Table 3: Atomic concentrations of CMFO films grown by PLD from a sintered powder target on both STO 111 and STO 100 substrates

EDS results, shown in Table 3, show elemental concentrations within 1% of the desired results. This is well within the error of the measurement which gives solid evidence that the PLD deposition resulted in direct transfer of atomic concentrations from the target to the substrate.

SEM images showing morphology of the films varied from sample to sample. The main factor of these changes was the substrate which was used.

It is important to note the difficulty at gaining high resolution SEM images from ferrite thin films grown on highly insulating oxide substrates. SEM images rely on the collection of backscatter and secondary electrons resulting from the electron beams interaction with the surface. The best images from SEM are those from surfaces that have high conductivities (large
carrier concentrations and mobility’s). Highly insulating surfaces such as those being images here, result in bright fuzzy unresolvable images. This is because of a high degree of negative electron charging on the surface. These charging regimes are essentially regions where electrons, or charge, are building up on the surface without anywhere to go. This results in very high backscatter and secondary electron signals from the surface, flooding the detectors. This makes imaging of the topology of the surface highly difficult because the charging hides any conducting features that may exists. This is why charging can even make it very difficult to image conducting nanostructures if they are on a highly insulating substrate material.

The structure of the target device depends of the fabrication of a discontinuous layer of CMFO in order for electron flow to still be attainable between the BFO under layer and the electrodes. This is why the CMFO films were all grown ultra-thin and imaged on different substrates.

Figure 22: SEM micrographs of (a) CMFO on glass slide (b) CMFO grown on Si (111). Both samples were grown at the same time for 20min, at 10Hz, 500°C and 1mTorr pressure (20% Ar and 80% O₂)
The samples grown for absorption measurements were grown on glass slides and an SEM micrograph of the surface is shown in Figure 22(A). For the most part the glass slide samples had very uniform film growth and few discrepancies in the surface (in this image three features were found simply to show that the image was focused as much as possible). In the example of Figure 22 the samples were grown at the same time on two different substrates at 500°C. Growth temperature of any higher than 500°C resulted in melting of the glass slide and this is why the growth was done at this temperature. The sample grown on Si (111) showed self-assembly of nanoparticles shown in Figure 22(B). In an attempt to increase the size and/or amount of nanoparticles from growth on Si (111) the temperature was increased to 900°C. This higher temperature introduces a higher degree of atomic mobility to the system and will result in higher particle growth rate. The SEM images obtained from this growth are shown in Figure 23. The nanoparticles showed a size distribution of roughly 20-50 nm in diameter. Under close inspection one can see that the nanoparticles are also highly faceted. Some even show a clear triangular geometry. This indicates a strong tendency for epitaxial alignment with the underlying Si (111) crystal geometry. It also proves that increasing the growth temperature resulted in higher atomic mobility and an increased crystallization rate.
This faceting and alignment with the substrate also lends some explanation to their formation. These nanoparticles seem to be created by a well-known self-assembly technique of lattice mismatch. This technique involves the selection of a crystalline substrate material that has a lattice parameter that is differing from that of the film. Due to this a strain is created between the two materials and this stresses the epitaxial growth of the film. This causes the material grow discontinuously by coalescing into clusters. Also witnessed if that these clusters will often
nucleate at specific lattice coordination sites on the substrate. The lattice mismatch between CFMO (8.526Å) and Si (111) (7.679) is 9.9% which is more than enough for this growth mode to dominate.

Figure 24: SEM images of CMFO growth on Si (111) for 40min, at 10Hz, 900°C and 1mTorr pressure (20% Ar and 80% O₂). Circled are large faceted triangular nanocrystals. These features are fewer in number than previous samples but have more distinguished features.

To further understand this growth mechanism another growth was performed with double the growth time (40min). In this sample the longer growth time has resulted in large and clearly
faceted crystalline geometry’s. The crystals that showed this preference for triangular facets are 150-200nm in equilateral side length.

Also evident in this sample are a smaller overall number of crystallites. The longer growth time has allowed the faceted crystals longer to grow in size at the expense of any smaller particles around them. This process of particle coarsening is often referred to as Ostwalt ripening, where high mobility allows larger particles to grow at the expense of smaller ones, decreasing the number and size of smaller particles and increasing the diameter of larger ones.

**AFM of top CMFO layer of full device**

These examples of self-assembly of nanoparticles on a lattice mismatched Si substrate lend hope to the finding of nanoparticulate discontinuous growth on BFO thin films in the devices fabrication. So finally the morphology of the top CMFO layer of the full trilayered device was characterized by atomic force microscopy (for specific growth conditions refer to device fabrication section).

For this study the BFO layer was deposited for 45min and the CMFO layer was deposited for 5 minutes (Figure 25). Using the deposition rate calculated by XRR the CMFO layer has a thickness of about 2.4nm. The nanocrystals/particles shown on the surface have a feature height of 2.5-4nm. This agrees closely with the deposition rate measured for CMFO and points at the layer shown in the AFM images to be fully constituted of the CMFO and not the underlying BFO.

The morphology of the CMFO film is indicative of the Volmer-Weber growth mode described in detail in past literature for ferrite thin film growth (20). Here Volmer-Weber island
growth has served to create feature sizes that are taller than the thickness of a continuous thin film of the CMFO layer (see Figure 25). This proves that vertical growth of the Volmer-Weber island was preferred over epitaxial nucleation and growth to the BFO underlying layer. This discontinuous layer helps to explain where the Ti/Au electrodes make contact to the underlying ferrite bilayer and also lends to evidence for where the charge is traveling during device exposure to visible light. Since the layer is not a uniform film the Ti/Au contacts must make contact with the underlying BFO layer.
Figure 25: (A) Layer device structure diagram (B) AFM images and 3d topography rendering of CMFO layer. AFM images of CMFO layer grown on BFO thin film (all on STO 1 0 0 crystal substrate)
**XRD of CMFO films grown on glass**

To probe the crystal structure of films x-ray diffraction (XRD) was used to probe the crystal structure of the films. In XRD the sample is irradiated by x-rays and the crystals constituent atoms scatter the incoming beam in different directions. The electrons surrounding the atoms in the crystal are what scatter the x-rays and in collecting the scattered radiation at a variety of angles we can gain a 3 dimensional map of the electron density in the system.

An x-ray diffractometer used on thin film samples serves another purpose in that x-ray reflectivity (XRR) can be performed. With XRR the x-ray beam is moved to irradiate the surface at very small angles. At these angles x-rays will reflect back and forth between the film and substrate interface and the top surface of the film. This creates an interference fringe pattern in the diffractogram. Using the distance between these fringes the thickness of the sample can be determined. This is an incredibly useful technique for these films in particular because it works best at very thin sample thicknesses (~5-50nm depending on the sample roughness).
Figure 26: XRD and XRR of CMFO thin film grown on glass substrate. Note the large background signal in the XRD graph (top). This is from the amorphous glass used as the substrate. The peaks are from the crystalline CMFO grown on the surface. Fringes in XRR graph are what are used to calculate the thickness of the sample (bottom).

Figure 26 shows the XRD diffractogram for a CMFO thin film grown on a glass substrate. Since CMFO has been largely unstudied a reference for peak positions in research literature could not be obtained. Therefore the XRD results, computations and comparisons were based on JCPDS of Iwakiite MnFe$_2$O$_4$ (MFO), PDF #38-0430. This PDF was chosen because cadmium manganese ferrite with a Cd concentration of x = .3 can be looked at as a cadmium doped manganese ferrite crystal. Also checked for correlation was PDF #10-0319 for the cubic form of MnFe$_2$O$_4$ (Jacobsite), but many of the peaks are shifted from my peaks to a higher θ ruling it out as a candidate for the crystal structure. The tetragonal crystal structure is also hinted at in the theory (19). Mn$^{3+}$ is a John-Teller ion which will distort the spinel structure. The Cd(Mn, Fe)$_2$O$_4$ was found to be elongated by the theory paper in the c-axis with $c/a > 1.0$ in all compositions ($0 < x < 1.0$).

By using the tetragonal MnFe$_2$O$_4$ PDF and Jade software, a calculation for the density of the CMFO film was executed. The density of the film came to 4.943 g/cm$^3$. The density of the
MFO in the PDF is 4.85 g/cm³. The difference between the two is reasonable because substitutional Cd atoms taking the place of Mn atoms in the lattice are larger. This also could explain why the lattice constant, “c”, is larger (see Table 4). The software calculated the lattice constant with 3 peaks, (2θ = 34.735, 34.915, 42.370). Furthermore these values agree closely with the theory paper by Min Feng et. Al. in 2011 (18,21,22). They calculated that CMFO has a cubic lattice constant a = 8.573 Å. Our crystal is very close to this, but slightly elongated along the c axis to be quasi-tetragonal as noted above.

XRR was also obtained for many of the samples (see Figure 26). This is what was used as a benchmark for the thicknesses stated in all of the material in this dissertation. Using XRR on the sample shown above, the calculated thickness came to be roughly 33-45nm. The range of values for the sample thickness is due to errors in XRR that come about because of sample surface roughness. For epitaxial films the measurement is highly accurate, but for our more rough samples grown on glass slides that are not very flat on the micron scale the error can be large. Using an average of different thicknesses for different samples I attained a deposition rate of .24 nm/min. This is also roughly the same deposition rate calculated for BFO samples as well and was used to estimate the BFO layers sample thickness. Since these films are so thin many of the samples were below the limit for XRR films with thicknesses below 5nm could not be measured and instead the deposition rate was used to calculate the thickness.

<table>
<thead>
<tr>
<th></th>
<th>MFO PDF</th>
<th>CMFO Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>4.85 g/cm³</td>
<td>4.943 g/cm³</td>
</tr>
<tr>
<td>a</td>
<td>8.59 Å</td>
<td>8.526 Å</td>
</tr>
<tr>
<td>b</td>
<td>8.59 Å</td>
<td>8.526 Å</td>
</tr>
<tr>
<td>c</td>
<td>8.54 Å</td>
<td>8.6615 Å</td>
</tr>
</tbody>
</table>

Table 4: Table of lattice calculations done with Jade software based off of JCPDS of Iwakiite MnF₂O₄ (MFO), PDF #38-0430.
Optical Absorption Measurements of CMFO films grown on glass

To determine whether CMFO is has a narrow bandgap appropriate for the solar spectrum optical absorption measurements were done on samples grown on glass. Those wavelengths of radiation that are absorbed by the film are a direct indication of the bandgap of the material. The physical process is a direct energy transfer from the radiation to the electrons in the system.

Figure 27: Simple schematic explanation of the bandgap in a semiconducting material [http://www.perkinelmer.com/Content/applicationnotes/app_uvvisnirmesurebandgapenergyvalue.pdf].

Figure 27 shows a general representation of the energy distribution versus the density of states in a semiconducting system. Irradiating a material such as this with an array of different wavelengths (energies) of radiation can result in either transmission through the material, reflection off the surface or absorption. The tendency is for this absorbed energy is to go to the electrons in the matter because the electron specific heat is much lower than that of the atomic
lattice, but this does not happen in most materials. In order to absorb the incoming radiation there needs to be an available energy band for the electron to exist in. For a metal the electrons already exist at all energy levels from the valance band up to the conduction band. The next place for electrons to go would be out of the material completely as a spark once the radiation energy is high enough to exceed the materials work function. Unlike a metal, in a semiconducting material there are forbidden energy bands where the electron cannot exist. For this reason an incoming radiation beam must be high enough to excite electrons from the valence band to the conduction band in order for it to be absorbed. A material that has a narrow bandgap in the visible is highly suitable for photovoltaic applications because it can absorb the most intense of the spectral radiation from the sun.

Absorption measurements were done via relative transmission optical spectroscopy (UV-Vis). The transmission was measured with an Ocean Optics USB4000 Spectrometer coupled with halogen lamp source. Optical fibers were used to both source and collect light within close proximity to the samples. Also used was an iron core magnet to test the absorption change with applied magnetic field of 1000Oe to the device.

Using the Ocean Optics software a rigorous process was used to obtain the absorption curve for samples of CMFO grown on glass slides (for growth conditions refer to CMFO thin film fabrication section). For these measurements the reflected light was assumed to have relatively the same spectrum as the light transmitted. This needs to be done because, since the samples are grown on glass most of the reflected light (which is very little) is from the glass slide backing. All attempts to separately measure the reflections of the glass substrate and subtract it from that of the sample resulted in intensities lower than the resolution of the system. As a result the reflection of the CMFO film was determined to be negligible.
The process method used was to first collect a dark background with the light source turned off. Then a reference spectrum with the sample removed from the holder and the source turned on was stored. Then the transmission through the sample was collected. This transmission plot was transformed into the absorption seen in Figure 28 by dividing by the reference spectrum (both the transmission and the reference were minus the dark background). Then the same process was done to measure the spectral absorption of the glass substrate. The final absorption of the sample was then plotted minus the absorption of the glass substrate in Figure 28.

Figure 28: Absorption curve for CMFO grown on a glass slide obtained by relative transmission optical measurements.
The inset of Figure 28 shows the absorption curve as a function of photon energy. From this curve we can deduce the optical bandgap via the Tauc method. The Tauc method is mainly used for determining the bandgap of amorphous and nanocrystalline materials (see Figure 29).

Since the CMFO thin films pose a large amount of localized photon scattering a clear bandgap edge is not evident in the absorption plot. Instead the Tauc approximation can be used to draw a tangent from the linear region in the absorption and deduce the bandgap from its intersection with the x-axis. Use of this approximation to calculate the gap, shown in the inset of Figure 28, resulted in a bandgap of ~1.37eV. This number agrees closely with the 1.3962eV gap calculated in the theory for Cd$_{1-x}$Mn$_x$Fe$_2$O$_4$, x = 0.25 (18).
This bandgap measurement was consistent with an array of different sample thicknesses (Figure 30). In the plot we can see that the bandgap is 1.37-1.4eV for most of the samples. However, for the thinnest of the sample thicknesses, the trend seems to show an increase in bandgap with a decrease in sample thickness (with only a couple outliers). This could be evidence of a tendency toward quantum confinement for the smaller thicknesses and perhaps the formation of quantum dot nanoparticles. Though there might be nanoparticles at these thicknesses evidence of such was unattainable via SEM imaging because of the small sizes and high degree of charging on the surface. Future studies by AFM might show that these samples grown on glass slides do in fact have confined nanoparticles on the surface. It is also important to note that for samples of thicknesses below 1.2nm the absorption intensity was too low to measure with the current instrumentation and also could have contributed to the apparent increase in bandgap measured for the thinnest samples.

**Figure 30:** A plot for the optical bandgap measurement for an array of CMFO sample thicknesses. At the smallest of the thicknesses we can see an increase in the bandgap for a few of the samples, perhaps indications a tendency towards nanoparticles and quantum confinement.
This finding marks the discovery of a ferrite with an absorption greatly in the visible. Other ferrites, such as BFO at 2.67eV (23), have much larger bandgap energies. This, in itself, is an important result to the field because it puts the possibility for ferrite photovoltaics on the map for energy and device research, (see previous sections for discussions on device theory and structure for more on this).

**BFO Films Characterization**

BFO films were grown and characterized by VSM, XRD, EDAX, UV-Vis absorption and PV Hysteresis loops. The results of all these experiments agreed closely with past literature and theory. SEM images were also done that showed a high degree of charging and a lack of strong features to note on the sample surface.

**Magnetic Characterization of BFO Films**

Magnetic measurements of BFO films were initially taken in much the same manner as those for the CMFO films accept initial measurements revealed a moment too low for the Lakeshore VSM to measure. For this reason efforts to characterize the room temperature magnetic characteristics were transferred over to a Quantum Design SQUID (superconducting Quantum Interference Device) magnetometer. Results of a hysteresis run out to 1 tesla are shown in Figure 31. The film for this example was grown by PLD for 1hr at 900°C, with a base pressure of 1.6x10⁻⁶Torr and a 50mTorr working gas pressure of O₂.
Figure 31: SQUID magnetization measurement on a BFO thin film grown on STO (110). PLD deposition was done at 900°C, a base pressure of 1.6e-6 Torr, 50mTorr working pressure of O₂ gas for 1hr.

The top graph in Figure 31 shows the raw data obtained from the magnetometer. The bottom graph shows what the graph looks like after subtracting the diamagnetism of the STO substrate. This diamagnetism was estimated by fitting the two outer ends of the curve to a linear fit. Then the slopes of these two linear fits were averaged and a line function representing the diamagnetism was subtracted from the whole curve giving what is shown in the bottom graph. This process is a typical procedure for all magnetic measurements of these thin film specimens. The diamagnetism of the substrate material must be subtracted to show the hysteresis of the magnetic component of the sample. This way we can accurately estimate the $M_s$, $H_c$ and $M_r$. The
moment in the second graph was also normalized to the estimated volume of the film (based on a thickness of 21.6nm). The estimated volume was 1.944x10^{-13} \text{m}^3 (as shown on the bottom graph inset). The obtained values for H_c and M_s agree closely with the literature of previous magnetic measurements on BFO which is known to be a soft antiferromagnet (24).

**XRD of BFO Thin Film layer**

The crystalline characteristics of the BFO layer and its epitaxial relationship to the underlying STO 001 substrate were determined by XRD of the thin film bilayer of both BFO and CMFO. The diffraction patterns were compared to previous studies on BFO thin films crystal structure when grown on STO (100).

**XRD of BFO + CMFO Device**

![XRD graph of BFO thin film grown on STO (100)](image)

**Figure 32: XRD graph of BFO thin film grown on STO (100)**
Figure 32 shows the diffraction data from a BFO + CMFO film bi-layer. The CMFO thin film is too thin (~4nm) for any strong peaks to be evident. The BFO peaks though are labeled on the graph. These peak positions agree closely with literature where BFO films were grown on STO (100) substrates (25,26,27). They also show relatively sharp BFO peaks which indicate fairly large crystals. This point shows a higher than typical degree of epitaxial growth on the substrate. The narrower the XRD peaks the larger the crystallites. This is because defects in the crystal structure, such as grain boundaries and crystal boundaries, tend to scatter the x-rays causing a broader peak around a specific crystal plane orientation in 2θ. High crystallinity is a favorable result for the BFO layer in the device. It is important that the BFO films are grown under the proper conditions to mimic those crystalline characteristics achieved in other papers. The reason is because other papers show that, with the right crystalline characteristics, ferroelectric polarization will increase and domains will form (see previous sections for discussions on device theory and structure for more on this). These domains increase the electric polarization in the films, leading to a higher open circuit voltage and therefore a higher amount of photo induced charge carriers being used for power generation rather than recombining with their counterpart holes.

**Ferroelectric Characterization of BFO films**

Like a ferromagnetic material does with a magnetic field, a ferroelectric can be polarized by an external voltage to have a spontaneous electric field (see background section on ferroelectrics). As seen before to characterize the spontaneous magnetization in a ferromagnetic sample an external magnetic field is applied to the sample. Then the magnetization is plotted at
the external field is ramped from negative to positive values, then back again. A ferroelectric material’s spontaneous polarization is characterized in much the same manner. Instead of the sample being exposed to an external magnetic field the ferroelectric is affixed with electrodes and a large electric polarization field is applied to the contacts. Then the polarization voltage is ramped from positive values down to negative values, then back again. Along the loop, from the same contacts, the samples resultant polarization is measured in tandem with the application of the polarization voltage. These sample polarizations are plotted as a function of the applied poling voltage. Due to the difference in the physical processes there are a couple other parameters that can change the resulting hysteresis loop though. First is the initial poling of the sample. Often times an initial poling voltage higher than the intended starting poling voltage for the hysteresis sweep can be used to increase the ferroelectric response and squareness of the hysteresis loop. Second is the time constant which is associated with the period for the hysteresis sweep. For reasons having to do with the nature of a ferroelectric sweep rate of the poling voltage can affect the look of a resulting hysteresis curve to the point where, if its value were too small or too large, the loop will not show the intensity of the spontaneous polarization accurately. These two parameters must be varied to find the best conditions to obtain a highly square, clearly open, PV hysteresis curve.

To characterize the polarization of the BFO films PV measurements were taken across the same interdigital electrode pattern as used in the final device design (see fabrication section for details on interdigital electrodes). Polarization measurements were taken out to voltages of 500V. Higher polarization are technically possible with this electrode configuration on BFO because dielectric breakdown wouldn’t happen until much higher potentials (>1kV). However, when larger potentials were tried, degradation of the Ti/Au contacts prevented the collection of a
good PV loop. This is why application of a high initial poling voltage could not be performed to try and reach a better hysteresis result.

**Figure 33:** PV loops for BFO device (Ti/Au electrodes on a BFO thin film) using different time constants, $\tau$.

Figure 33 shows PV loops for the BFO thin film grown on STO (100) across Ti/Au interdigital electrodes patterned on the surface via photolithography. The clear hysteresis in the PV loops indicates that there is an internal spontaneous electric field in the film. The changing of the shape with different time constants, $\tau$, is typical for PV loop measurements for ferroelectrics. Decreasing the time constant also decreases the remnant polarization in the specimen. Increasing the time constant increases the remnant polarization in the specimen, but also increases drift of the top of the loop to higher polarizations. The ideal polarization loop looks like a square with clear saturation and switching values. This loops deviation from ideal and apparent roundness
could be due to a number of factors including leakage of current between the electrodes, crystalline quality of the film, deviations from stoichiometry particularly in oxygen deficiency and the shape of the interdigital electrodes and how they affect the distribution of the electric field in the sample. Verification of the electric polarization in the BFO thin film is vital to proving the theoretical operation of the device. These hysteresis loops lend proof to the presence of an electric field in the BFO. Further study of the BFO films and measurement of the loop could lead to a better acquisition method for determining more accurately the strength of the electric field in the specimen. For this proof of concept it suffices to show that the material is ferroelectric and possesses a spontaneous electric field suitable for charge manipulation in the photovoltaic.
PHOTOVOLTAIC DEVICE FABRICATION

The device is essentially a ferrite thin film bilayer grown on SrTiO$_3$ single crystals. The single crystals used for the substrate were 1 0 0 orientated and 1sp polished after cleaving (purchased from MTI crystals). This crystal orientation was chosen because when BFO is grown by PLD on these substrates the result is a ferroelectric domain pattern that serves to increase the internal electrical field of the film (28). Also found was that CMFO has the best magnetic characteristics when grown on STO 100 single crystals (see magnetic characterization section).

The process starts with the PLD growth of the BFO + CMFO bilayer. The initial BFO growth was done at temperature of 650°C for 45min at a pulse rate of 10Hz. For device #1 this was the only ferrite layer deposited so that it may act as a control in photovoltaic testing against the characteristics of the BFO + CMFO bilayer device. For device #2, however, another layer of CMFO was deposited in-situ directly after the BFO layer at 650°C and 10Hz, but for only 5min. After both layers were deposited the substrate was cooled in the 100mTorr O$_2$ atmosphere to 80°C over 30min. Future experiments might extend this cool down time to try and decrease the number of oxygen deficiencies in the system. For more on this and why it is important, see the section on photocurrent and photovoltage measurements.

A background working gas of O$_2$ was used at a pressure of 100mTorr for the entire length of heating, cooling and growth in the chamber. The reason for the oxygen environment is to keep the oxygen atoms in the lattice at stoichiometric values during the deposition. Essentially, this turns the PLD process into, what many like to call, RPLD (Reactive Pulsed Laser Deposition)
because the oxygen is reacting with the free unbounded metal atoms to maintain the oxide stoichiometry in the ferrite.

On top of this bilayer are interdigital Ti/Au electrodes patterned on the surface by photolithography. Patterning was done by first spinning Shipley 1827 photoresist on the surface and post baking the layer on a hotplate at 100°C for 1min. Then a photomask, (see Figure 34), was placed on top of the sample and exposed to UV light for 35 seconds. The sample was then developed by dipping it in 319 developer solution for 1min and rinsed in DI H₂O for 3minutes.

![Mask used for photolithography of interdigital electrodes with dimensions.](image)

The spacing of the Ti/Au electrodes was .015cm. Varying this dimension should have an effect on the photocurrent and photovoltage and varying of this parameter might be a good study to do for future investigations.

The Ti/Au electrodes were grown by magnetron sputter of a titanium target with Au flakes placed on top of it (see Figure 11). The sputtering was done with an RF power source with a power of 50W for 15min. The working gas in the sputter was Ar held at 4-7mTorr.
Liftoff of the photoresist was then done by dipping the sample into 1165 solution for 2hrs at 80C. Then intermittent sonication in the 1165 solution was done at 1sec intervals to remove the remaining metal material between the electrodes.

To make electrical contact to the contact pads of the electrodes two gold wires were pressed into indium metal, which was then pressed onto the surface of the Ti/Au contact pad on the sample. A photo of the two devices (device #1 being the control with just BFO and device #2 being the BFO + CMFO) is shown in Figure 35. On a side note you can clearly see that device #2 appears darker than device #1. This clearly shows the large difference in visible light absorption between BFO and CMFO. Not only does the whole device appear darker but it does so with only a 2.5nm coating of the CMFO layer.

![Figure 35: Photo of completed photovoltaic devices next to a penny.](image)
Figure 36: SEM images of completed BFO + CMFO device surface. Image to the right shows the surface of the CMFO in between the electrodes. The morphology points to a tendency to nanoparticles with enough voids to allow for conduction pathways between the electrodes and the BFO under layer.

Figure 36 shows a couple SEM images of the completed device. The left image shows the electrodes on the surface while the right image shows a higher magnification of the space between the electrodes. One can see subtle traces of nanoparticles, or nanocrystals, on the surface. This helps to confirm the presence of the discontinuous morphology of the CMFO that was already imaged in the bilayer sample using AFM (see Figure 25).
Figure 37: Fabrication process steps for both devices

Device #1 - BFO

STEPS:
- PLD on STO <100> BFO from sintered target. 45min, 650C, 100mTorr O₂, 10Hz --- Cool for ~.5hr to 80C ---
- SPIN Shipley 1827, post-bake for 1min @100C, Expose for 35sec, Develop in 319 for 1min, Rinse in H₂O
- Sputter Ti/Au electrodes @ 50W for 15min, 4-7mTorr Argon
- Lift-Off in 1165 for 2hr, then sonicate in lift-off intermittently (1sec intervals)
- Remove from lift-off, rinse in DI, Then rinse in IPA
- PRESS Indium onto contact pads with Gold wires
- ***POLE then TEST

Device #2 – BFO/CMFO

STEPS:
- PLD on STO <100> BFO from sintered target. 45min, 650C, 100mTorr O₂, 10Hz
- In-Situ PLD CdMnFeO from sintered target, 5min, 650C, 100mTorr O₂, 10Hz --- Cool for ~.5hr to 80C ---
- SPIN Shipley 1827, post-bake for 1min @100C, Expose for 35sec, Develop in 319 for 1min, Rinse in H₂O
- Sputter Ti/Au electrodes @ 50W for 15min, 4-7mTorr Argon
- Lift-Off in 1165 for 2hr, then sonicate in lift-off intermittently (1sec intervals)
- Remove from lift-off, rinse in DI, Then rinse in IPA
- PRESS Indium onto contact pads with Gold wires
- ***POLE then TEST
PHOTOVOLTAIC DEVICE TESTING

The devices were tested using an Oriel solar illuminator. The illuminator was calibrated with a CEM Solar Power Meter. In all diagrams the power units of SUNS correlates to the following metric; \([1 \text{ SUN} = 1000 \text{ W/m}^2]\). All measurements were taken immediately after poling the device. A separate Stanford Research Systems high voltage power supply was used to pole the devices at 150V for 15min.

Photocurrent Measurements

Initially, without any external poling, the devices show little to no photocurrent. The degree that this affects the photocurrent is shown in Figure 38. This shows the virgin devices photocurrent as function of poling voltage. The graphs data was collected starting with the virgin untested device. After the device is fabricated the initial photocurrent achievable is little to none, but since the accuracy of the equipment could not read such a low value there isn’t a data point for zero poling voltage. The reason why the photocurrent is nonexistent with the virgin device is because the BFO ferroelectric has yet to be polarized. This is one large difference between the workings of a ferromagnet and a ferroelectric. It is that, without an initial poling, there is no measurable spontaneous electric field in the sample, as opposed to a ferromagnet whose spontaneous magnetic polarization is created by the crystalline symmetry and often has a measurable polarization even without initial magnetization.

The curve for the virgin device polarization as a function of photocurrent shows how with higher poling voltage a higher photocurrent is achievable. This is because the higher the poling
voltage the larger the spontaneous field that exist in the sample when the voltage is removed. You’ll notice though, that even the highest photocurrents measured aren’t as high as witnessed in Figure 40. This is because the devices seem to have a break-in period whose length is yet to be determined. The more the devices were tested the better they performed, but this relationship seemed to plateau after a few days of testing. Further investigations might look more into this to determine a process for breaking in the devices before testing.

![Graph: BFO + CdMnFeO Photo-current vs Poling Voltage (Virgin device initial poling)](image)

**Figure 38:** Virgin device #2 photocurrent as a function of poling voltage. This was taken by first poling for 10min at voltages from 0 - 150V, then turning on the illuminator, waiting 3min, then recording the datapoint for current.

It is important here to note how the photocurrent densities were calculated. Photocurrent density is the normalized photocurrent used as the figure of merit for photovoltaic devices. This density is typically calculated by dividing the current obtained from the device by the surface...
area of the device exposed to the light. However this typical treatment is used for junctions whose current runs out of plane, meaning that the current flows through the layers from the bottom layer towards the top layer (or vice versa). For this case the electrodes are planar and the current flows in plane with the film. The interdigital electrodes cause the majority of the current to flow across the overlapping digits as shown in Figure 39. In light of this photocurrent density (J) was calculated using the equation derived in Figure 39.

Using this calculation for the current density of these devices (with \( A = 1.2 \times 10^{-6} \text{ cm}^2 \)) the max value from the BFO + CMFO device was 14.1 mA/cm\(^2\). This value is on the same order as the current state of the art solar harvesting technologies (with silicon being around 30mA/cm\(^2\)). More importantly it is very close to competing technologies to silicon that have been in development for many years such as organics and dye sensitized solar cells whose photocurrent densities are around 10 – 15 mA/cm\(^2\).
An important thing to note when comparing these values for photocurrent density to other technologies is the others are calculated using the whole surface area of the device for the photocurrent density. In principle, miniaturization of the devices shown here could increase the photocurrent and photovoltage with further testing and study. Also, for a proof of concept to show such a large photocurrent density on only the first iteration of the device design is a profound step towards the realization of a ferroelectric photovoltaic capable for use in solar harvesting.
Figure 40: Photocurrent measurements of both BFO device #1 and BFO + CMFO device #2. (A) shows photocurrent measurements over 15 minutes of acquisition on a log plot to show the order of magnitude increase in photocurrent between the BFO device and the CMFO device. (B) shows the switching behavior of the photocurrent from both devices over 10 minutes. Note that the initial value of the photocurrent is not zero in either graph because there is a remnant current after poling. It aligns directly to the beginning of the decay at the other end of the graph.

Figure 40 shows the photocurrent measurements of both devices. The current measurements were taken using a Keithley 2182 Nanovoltmeter and collected using Labview. The current was measured by measuring the voltage drop across an in series 32.88 kOhm shunt resistor. Different resistor values were used without large changes in the photocurrent being measured. Future measurements of such devices might look into decreasing the resistance of this shunt resistor to increase the overall photocurrent measured.
In all of these experiments there was the hurdle of defining the data while taking into account the time dependence of the photocurrent. The data in Figure 40 and Figure 41 were taken immediately after poling the device. Figure 41 shows best how the photovoltage goes over an initial increase after the illuminator is turned on. Initial spikes are always evident once the light is turned on as they are shown to go off the scale. After the initial spikes the voltage increases for about a minute but then its second derivative changes sign and the photovoltage starts to flatten out and decrease. The trend here has been explained in previous publications on the photovoltaic characteristics of BFO and is said to be due to oxygen vacancies in the film. Further study into growth procedures for the BFO film might lead to decreasing this decay rate.
In analyzing the photovoltage curve in Figure 41 one might notice that the BFO device shows a higher photocurrent than that which incorporates the CMFO layer. This is a viable result explained by the lower resistivity of CMFO and the larger carrier concentrations present in the BFO + CMFO device once the light is turned on. This can also be interpreted as “leakage”. But for these devices and for a solar harvesting application in general, leakage may not be a bad thing. The higher the carrier concentration in the device the more leakage it will experience, but also the higher the photocurrent that the device will generate. On the other hand in order to continually keep the photo-induced charge carriers flowing and not recombining you need the
high internal electrical field provided by the BFO; which would in turn reduce the leakage. To determine which parameter has a larger effect on the total power of the cell (open circuit photovoltage or photocurrent) further experimentation with interdigital electrode spacing might lead to a conclusion. Theoretically by increasing the distance between the electrodes the effective electric field for charge carrier transport should increase. By decreasing the spacing between the electrodes the photocurrent should increase and the open circuit voltage will decrease. By generating samples with an array of electrode separations one should be able to determine a value that yields both the highest photocurrent and the highest photovoltage.

Figure 42: Comparison of the best observed open-circuit voltage (Voc) for different photovoltaic materials as a function of their band gap (1). Shown are the band gap value (black line); the open-circuit-voltage limit due to radiative recombination (gold line); the open-circuit-voltage limit due to radiative recombination, including potential fluctuations with an amplitude of $\sigma E = 100$ meV (dashed green line); and a line indicating half the band gap value (dashed red line). CZTS denotes $\text{Cu}_2\text{ZnSn(S,Se)}_4$. The red circles denote polycrystalline materials, and the blue circles denote crystalline materials.
The role of non-radiative recombination in photovoltaic materials can be analyzed by plotting the observed open-circuit voltage, \( V_{oc} \), values of devices on the basis of different materials versus the bandgap. In Figure 42 we can see these points plotted for different materials and lines that denote the limit based on theory (gold line) for the span of band gaps shown. Shown in Figure 41 is the \( V_{oc} \) measured for BFO of \(~0.97\)V after device poling, and this value is plotted outside the graph in Figure 42 above. Though it is off the chart one can see that the spontaneous electric polarization in BFO, plotted with its band gap of \(2.67\)eV, is higher than most traditional semiconducting materials. One can also see that at such a large bandgap the theoretical open circuit voltage limit due to radiative recombination is higher than \(1.7\)V. This value for \( V_{oc} \) is from this proof of concept and with tuning of growth conditions this value should increase substantially to this limit as crystal defects and inhomogeneities in electronic interfaces are minimized. Essentially, this large measured \( V_{oc} \) shows how a ferroelectric has the potential to circumvent the recombination of holes due to non-radiative recombination because even with the first proof of concept approach an open circuit voltage comparable to the best semiconducting p-n junctions is achievable.
Measurements Varying Light Power

Figure 43: Photocurrent versus solar illuminator light power

Also measured was the dependence of the solar simulators light power on the photocurrent. Often time photovoltaics are measured under multiple suns of power to try and maximize their photocurrent generation potential. Here the power is varied from .5 SUNS to 2 SUNS and the photocurrent is measured. An increasing photocurrent can be seen with the increasing power. This is expected because as light intensity increases the probability of an excitation also increases. This correlates with a larger number of photocarriers being carried by the spontaneous electric field in the system. The opposite of this is seen in the trend of open circuit photovoltage with illuminator power.
Figure 44 shows the dependence of open circuit photovoltage ($V_{oc}$) on light power. Unlike the photocurrent the photovoltage decreases with increasing light power. This indirect relationship to light power is understandable because, even though current increases as seen in Figure 43, the resistance to charge motion (mobility) stays the same. Therefore the rising current drives the voltage down because the intrinsic resistance does not change.
**I – V Measurements**

![I – V CMFO + BFO Device](image1)

![I – V BFO Device](image2)

Figure 45: I - V curves taken with light ON and light OFF conditions. The sweeps were taken by sourcing constant voltage.

Lastly IV curves were taken to determine the overall electrical properties of the devices. The IV curves were taken using a constant voltage applied to both contacts while measuring the current in a 2 point geometry but still using the interdigital planar electrodes. There were also two sweeps used for each device, one with the light ON and one with the light OFF. The results gave an offset IV curve for the light ON condition for both devices shown in Figure 45. Due to the high resistance of the ferrite system the light OFF condition shows a flat line close to zero for both devices. With a more sensitive IV setup it might be possible to resolve the behavior with the light off. This would give some insight into the conduction characteristics of the devices and the nature of the electrode to ferrite interface. But for the capabilities of this setup the light ON characteristics show a clear trend between -3V and 3V. Both devices show an offset curve towards the 4th quadrant. This is expected because with the light on there is a measureable current and a measureable voltage. It is also important to note that before running this hysteresis
the devices were polled in the positive direction, serving to offset the photovoltage to a positive value. For the CMFO + BFO device the zero voltage biased photocurrent is an order of magnitude larger than that for the BFO device, further verifying the measurements taken in Figure 40.
CONCLUSIONS

This thesis explores a new approach to the realization of a viable photoferroelectric photovoltaic device for solar harvesting applications and also studies a novel material to demonstrate such a concept.

For integration of a narrow bandgap absorber material into a ferrite based photoferroelectric device it is desirable for it to be another ferrite. The study of cadmium manganese ferrite in its thin film form was studied for the first time in this work. Its magnetic and optical characteristics were determined after growth on glass slides. The films were grown by PLD and characterized by x-ray diffraction for crystalline characteristics, VSM magnetometry, EDAX for chemical composition, AFM for surface morphology and optical bandgap measurements were determined using the Tauc method on absorption curves obtained by relative transmission. Most notable of the results were those from the absorption measurements. Cadmium manganese ferrite proved to have a narrow bandgap of 1.37-1.40eV. This narrow of a bandgap is rare for ferrite materials and brings to light the possibility of photovoltaic devices based on ferrite materials for optical applications. Also notable were the magnetic properties obtained by VSM measurements. The coercivity and magnetizations obtained for the films were large compared to other semiconductor ferrites. Combining these properties makes for an interesting material system which has both a narrow bandgap and a measureable magnetization. It is also a complex oxide which has lattice size and orientation similar to other ferrites which are currently popularly being investigated for many applications.

Also investigated was the effect growing on other substrates such as STO 111, STO 100, Sapphire and silicon 111 has on the materials magnetization. These results showed that the film
had the highest squareness and largest magnetization when grown on strontium titanate (STO) 0 0 1 single crystals. This was a good result because the proof of concept also demonstrated in this study called for a heterostructure bilayer of CMFO and bismuth ferrite (BFO) grown on such a crystal (STO 0 0 1). It was also shown that when cadmium manganese ferrite is controlled to be very thin (1-2nm) on top of BFO 0 0 1 (epitaxial to STO 0 0 1) it forms a discontinuous nanogranular layer. For the purposes of this study a discontinuous layer was necessary for realizing this conceptual device design (shown in Figure 7).

Bismuth ferrite thin films were also characterized with the intention to determine both the epitaxial and ferroelectric characteristics of the film for incorporation in a proof of concept enhanced photoferroelectric thin film device. To probe the films qualities they were characterized by x-ray diffraction for crystalline characteristics and epitaxial relationship to underlying strontium titanate 0 0 1 oriented single crystal, SEM/EDAX for morphology and chemical composition, SQUID magnetometry for magnetic characteristics and P-V loop measurements to determine the ferroelectric nature of the films. The characterizations all summed up to show an epitaxial film which is weakly magnetic (antiferromagnetic) and containing a clear ferroelectric hysteresis indicating a switchable internal electrostatic polarization.

This thesis also explores the results of a proof of concept study for a photoferroelectric photovoltaic device design incorporating these two films. The concept for the device is novel in that it combines a narrow bandgap absorption ferrite with a wide bandgap photoferroelectric ferrite. The combination was grown in-situ by pulsed laser deposition in an oxygen atmosphere. On top of the heterostructure interdigital Ti/Au electrodes were pattern by photolithography and deposited by sputter deposition. A series of devices were fabricated with and without the
cadmium manganese ferrite layer. For photocurrent measurements it was conclusively shown that the cadmium manganese ferrite layer resulted in an order of magnitude increase in the photocurrent under simulated solar illumination (from $J = 0.9\text{mA/cm}^2$ to $J = 14.1\text{mA/cm}^2$). Crystalline silicon typically has a photocurrent density of $J = 28 - 35 \text{mA/cm}^2$, amorphous silicon of $J = 15 \text{mA/cm}^2$ and dye sensitized solar cells (DSSC) and organic solar cells in the range of $J = 13 - 17 \text{mA/cm}^2$. The photocurrent densities measured in this study are well within the range of current technologies that are in line to compete with silicon for their spot in many photovoltaics applications.
EQUIPMENT AND METHODS

SEM/EDAX:

SEM images in Figure 22, Figure 23, Figure 24 and Figure 36 were obtained using a Hitachi S-4800 Ultra-high Resolution Field Emission SEM. EDX measurements were done in-situ with SEM measurements with an EDAX Genesis 4000 X-ray chemical analysis system.

AFM:

For atomic force microscopy (AFM) of cadmium manganese ferrite thin film topography a Parks Scientific NX-10 AFM was used (Figure 25). 3d models of the topography data were rendered using “XEI”, an XE image processing program provided by Park Systems.
**Optical Absorption:**

Absorption measurements were done via relative transmission optical spectroscopy (UV-Vis), (Figure 48). A Hamamatsu L10290 halogen light source was used for illumination. The transmission spectrum was collected with an Ocean Optics USB4000 Spectrometer. Optical fibers were used to both source and collect transmitted light within close proximity to the samples. Spectrum analyses was done with the provided Ocean View data processing software from Ocean Optics (Figure 28, Figure 30).

![Figure 48: Experimental setup for optical absorption measurements](image)
**VSM:**

To measure the magnetic characteristics of the cadmium manganese ferrite samples grown on glass slides a Lakeshore 7400 series VSM (vibrating sample magnetometer) was used (Figure 21, Figure 15, Figure 18, Figure 19, Figure 20). For these room temperature measurements a Lakeshore 7400 series VSM system was used.

*Figure 49: Lakeshore 7400 series VSM system*
**SQUID:**

For magnetic measurements taken on low moment bismuth ferrite thin films a SQUID (superconducting quantum interference device) magnetometer was used (Figure 31). The RSO head was used for a room temperature hysteresis with the sample mounted in a plastic straw. The diamagnetism of the plastic straw and STO (strontium titanate) substrate was subtracted by estimating the linear contribution in the M v H loop at high fields.

![Quantum Design SQUID magnetometer](image)
**PLD Target Preparation:**

Preparation of target for PLD was done by ball milling constituent powders, axial pressing and then (for device and BFO depositions) sintering. Weighing of the powders was done with a Mettler Toledo PL303 high precision laboratory scale. Ball milling was done with a Fritsch pulverisette high speed ball mill in a sealed Teflon jar with steel balls (mixed in alcohol as a slurry). All pressing was done with a hydraulic Carver press and a stainless steel die set. Target sintering was done with a Sentro Technologies high temperature box furnace in a covered alumina crucible in air.

![Image of PLD Target Preparation equipment]

*Figure 51: (A) Fritsch Pulverisette ball mill (B) Die Set (C) SentroTech box furnace (D) Carver axial press*
Pulsed Laser Deposition (PLD):

Pulsed laser deposition was performed using a PVD Products NanoPLD system. The system is composed of a custom vacuum chamber coupled with a krypton fluorine (KrF) excimer laser. The laser is a Coherent technologies Thin Film Star Tuilaser (TES-100-248nm-CT-T V1.0). The chamber is equipped with rotating substrate and target and a programmable restoring laser mirror. Unique to this system is a radiatively heated substrate (heated by 6 halogen bulb heat sources).

Figure 52: PLD system
**P – V Loops:**

For measuring P – V loops of the bismuth ferrite thin films a Radiant Technologies ferroelectric testing station was used. The testing station was modified to allow for poling and measuring to be implemented through two wire contacts to the sample (rather than the typical out of plane device setup). Plotting and analyses of the loops was done with the Radiant Technologies provided Vision software.

![Radiant Technologies Multiferroic tester](image)

**Photovoltaic Measurements:**

Photovoltaic measurements were performed using an Oriel solar illuminator as a light source. Calibration of the light source was done with a CEM solar power meter. Initial poling of the devices was done using a separate Stanford Research Systems high voltage power supply. To measure the current a Keithley 2182 nanovoltmeter was used to measure the voltage drop across a 32.88 kOhm shunt resistor. To capture the data a labview program was made to interface with the nanovoltmeter via a National Instruments GPIB-usb adaptor.

![Photovoltaic measurements setup](image)
CITATIONS


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