ABSTRACT

KELLEY, KYLE P. Mid-Infrared Plasmonics in Cadmium Oxide Thin Films. (Under the direction of Dr. Jon-Paul Maria.)

Engineering light-matter interactions in the infrared spectrum is of keen interest to the materials science, photonics, physics, and biophysics communities. That interest arises from opportunities for advanced communication platforms, chemical sensing, optical characterization, energy harvesting, and catalysis. A key feature amongst these diverse applications is the central ability to confine light into localized physical geometries, and in some cases below the diffraction limit. Noble metals patterned or formed into nanoscaled shapes are perhaps the most common embodiment enabling this. In such cases, it is possible to couple light into localized surface plasmon polaritons directly from free space. However, the metal carrier concentration is fixed, thus one must use geometry to engineer the polaritonic response. While it is possible to access wide frequency spectrum, elemental metals can be lossy (due to low carrier mobility) which limits the quality factor of the excitation. Furthermore, such metallic structures typically feature dimensions on the order of several tens of nanometers, which presents practical challenges of patterning, particularly over larger areas. This combination of loss and processing expense introduce barriers to application and integration.

An alternative approach to photon compression can be appreciated in an epsilon near zero plasmon polariton mode (ENZ). This mode offers extreme sub-wavelength confinement of electric fields and can be realized in a thin slab of conductor bounded by a dielectric medium. This offers a lithography-free avenue to create structures that support these interesting modes, but unfortunately, the high carrier density of elemental metals requires that such layers be impractically thin, i.e., 2 nm, and the mode energies would be well outside of the IR spectrum. An interesting class of materials known as conducting metal oxides (CMOs) can provide the necessary electrical properties of an IR ENZ mode.

Facilitating this transition to CMO's for plasmonic applications requires significant materials development. Specifically, tailoring the electrical properties of CMO’s capable of IR plasmonics demands a delicate choice of material system, dopants, and synthesis method. The first section of this dissertation aims to provide a theoretical understanding of the previously mentioned ENZ mode and the desired electrical properties necessary to sustain low-loss, high quality plasmonics. Further, doped cadmium oxide is proposed as a feasible material system.

Previous work performed by Sachet et al. demonstrated that dysprosium doped cadmium oxide synthesized via molecular beam epitaxy (MBE) possess desirable electrical properties, most notably a high electron mobility, for plasmonic applications. However, the sophistication of MBE instrumentation presents a barrier for material implementation. As such, there is interest to explore if similar properties are achievable in alternative deposition methods. In this work, we studied
doped cadmium oxide synthesized from various sputtering techniques, i.e. RF and high-power impulse magnetron sputtering (HiPIMS), identifying sputtering as a practical alternative to MBE. Moreover, these techniques allowed for the exploration of alternative dopants for the cadmium oxide system which include yttrium, indium, tin, aluminum, cerium, and silver.

The flexibility offered from HiPIMS enables the development of unique multilayered structures. In this section of the dissertation, we determined multilayered homoepitaxial structures can be fabricated that support multiple ENZ modes in the mid-IR spectral range. The realization of multiple ENZ modes in a given system allows for new functionalities in wave-front engineering, tailored thermal emissivity, and extraordinary optics.

The final part of this dissertation examines the interaction of multiple plasmon polariton modes in multilayered homoepitaxial systems. When coupling ENZ and surface plasmon polariton (SPP) modes, a spatial dispersion of the two modes can be observed, producing new interesting physics. The ability to tune the coupling of the two modes allows for a mixture of desirable plasmonic properties - high electric field confinement and mode propagation. The mode mixing presented here is an advancement capable of paving the way to future light-matter interactions.
Mid-Infrared Plasmonics in Cadmium Oxide Thin Films

by
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DEDICATION

To my mother and father. Without you, this would not have been possible.
The author was born on April 10th, 1991 to parents Lynn A. Lee and Paul Kelley in the United States of America. He grew up in a small town in western North Carolina where most of his time was spent outdoors. In 2009, he decided to attend Appalachian State University in Boone, North Carolina where he studied Applied Physics. In 2014, he graduated with a Bachelors of Science focusing on thermal properties of organic solar cells under the supervision of Dr. Tonya Coffey. After graduation, he became a zip-line guide where he debated his career in science.

In Fall 2014 he was accepted to the Ph.D program at North Carolina State University and agreed to work under the advisement of Dr. Jon-Paul Maria. While pursuing his doctorate with Dr. Maria, he extensively studied light-matter interactions in doped cadmium oxide. More specifically, he explored various thin film deposition techniques and plasmonic phenomenon in the mid-infrared energy spectrum.

While science is a large part of Kyle’s life, he also enjoys having family and friends over for game night, riding and fixing motorcycles, canoeing and hiking, white-water rafting, and even lounging around a camp fire. He believes balancing his scientific life and personal life is the key to success.
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Introduction

1.1 Motivation for this Work

Plasmonics is an ever-expanding field in the forefront of physics and optical science that collectively brings together a number of disciplines. It spans materials science and electrical engineering, to fundamental chemistry in efforts to understand the interaction between electromagnetic fields and free electrons at metallic-dielectric interfaces and metallic nanostructures. The rapid growth of plasmonics in the scientific community can be attributed to the advancements in nanofabrication and thin film science, unraveling the realization that there are many unanswered questions and new phenomenon, ranging from tunable Rabi splitting and wave-front engineering to controlled thermal emission and sub-wavelength confinement.

The field of plasmonics is truly beautiful. Electromagnetic wave-electron interactions can be highly characterized and interpreted from Maxwell's equations, which is extremely powerful. With a basic understanding of electromagnetism and optics, one can begin to realize the possibilities and future applications of plasmonics. One aim of this dissertation is to provide a pathway for appropriate materials fabrication, and assist in an understanding of the current field of plasmonics as it can be extremely convoluted.

Historically, plasmonics have been discussed in the context of surface plasmon polaritons (SPP), which are bound electromagnetic surface waves that propagate along a metal-dielectric interface. As an incident electromagnetic wave with the electric field component in the plane of incidence impinges on a metal-dielectric interface, provided certain requirements are met, the incident electric field can excite the collective oscillation of delocalized electrons giving rise to SPPs. The propagating wave consequently has evanescent electric fields decaying in the metal and dielectric.

Surface plasmon polaritons have been primarily investigated in traditional plasmonic materials, such as silver and gold. However, these material systems are lossy due to their inherently low
electron mobilities, which has a strong impact on the plasmonic performance and light-matter interactions. To overcome these losses, the plasmonics community has pursued alternative routes such as introducing optical gain, plasmonic structure size and shape optimization, and using highly doped semiconductors\(^1\). Although these sophisticated techniques provide suitable solutions for plasmonics in the visible and ultra-violet (UV), the infrared still remains a challenge to address.

In the past decade, the plasmonics community has extended its search for low-loss infrared plasmonic materials to conducting metal oxides (CMOs). Some CMOs offer a range of tunable electron concentrations ranging from \(10^{18}\) to \(10^{21}\) cm\(^{-3}\), while maintaining relatively high electron mobilities. The diverse range of accessible carrier concentrations allow CMOs to span the entire IR with sharp plasmonic resonances. Using CMOs as efficient, low-loss systems for SPPs provides a pathway for a variety of applications, included surface enhanced Raman spectroscopy (SERS)\(^2\), high efficiency waveguides\(^3\), plasmon lasers\(^4\), sensors\(^5\), information storage\(^6\), etc\(^7\).

With that in mind, the most promising low-loss CMO for infrared plasmonics to date is cadmium oxide (CdO). Herein, we focus on the accessible electronic properties of cadmium oxide followed by unprecedented plasmonic properties and applications.

1.2 Historical Overview

The initial interest in surface plasmon polaritons was born from observations by R.M Wood in 1902 at Johns Hopkins University. He noticed that when irradiating a metal backed diffraction grating with transverse magnetic (TM) polarized light, the reflected light had extremely dark and bright bands seen in Fig. 1.1. He states "I am of the opinion that a study ... may throw some further light on the problem, which is one of the most interesting that I have ever met with", intriguing fellow scientist in the field. Although Wood published his findings and speculated on how the light and gratings interacted, he was still unable to formulate a clear answer to why this phenomenon was occurring. In 1907, Lord Rayleigh was the first to give this phenomenon a mathematical treatment describing the bands with a dynamical theory where the spacing and depth of the gratings is crucial.\(^8\)

Although Lord Rayleigh was able to mathematically predict an anomaly at a specific wavelengths, his theoretical understanding was still lacking. In 1941, Fano offered an alternative explanation. Knowing that the momentum, or wave vector, of the polarized radiation incident parallel to the grating will be increased in multiples of \(2\pi/a\), where \(a\) is the grating spacing, he believed that increasing the momentum of the incident radiation generates an evanescent field which will be diffracted into surface waves, or Sommerfeld's waves. He described these as "quasi-stationary waves which represent an energy current rolling along the surface of a metal", which was the first prediction of surface plasmon polaritons.\(^9\)

Not until the early 1950's, with the quantum mechanical descriptions from D. Bohm and D. Pines, was the first understanding of the surface waves accurately hypothesized and described. Circa 1950
to now, there have been numerous advancements in the field of plasmonics beginning a new era of light-matter interactions.\textsuperscript{10,11,12,13,14}

\subsection{1.3 Light-Matter Interactions}

Classically, light-matter interactions encompass the behavior of charged particles in the presence of an electromagnetic field. Numerous scientific fields and applications have branched from this topic, including light harvesting or solar cells, LEDs, lasers, magneto-optical traps, plasmonics, optoelectronics, etc. In the context of plasmonics, the study of light-matter interactions has been centered around understanding surface plasmon polaritons, which have been central to the fields development. Furthermore, surface plasmon polaritons provide a fundamental understanding of additional plasmonic modes, and is a key feature of this dissertation. Recall, surface plasmon polaritons exist at the interface between a dielectric and metal. Therefore, to begin understanding how surface plasmon polaritons and other polaritonic modes exist, we first need to understand how an electromagnetic wave propagates through a medium. As such, the dielectric function, which describes how an electromagnetic wave interacts with a material, is of detrimental importance.

In the context of metals, and conducting metal oxides, there lies a transition from negative to positive dielectric character. When the dielectric function lies in the negative regime (frequencies below the plasma frequency), the electrons in the system can respond fast enough to screen electromag-
netic waves, i.e. a reflective state. However, at frequencies above the plasma frequency, the electrons in the system cannot respond and electromagnetic waves can penetrate. This in turn means that over a range of frequencies, materials can have metal or dielectric character depending on their electrical properties. In the following derivations, it is assumed that we are operating at frequencies below the metals plasma frequency, satisfying the criteria for surface plasmon polaritons.

Finally, after establishing electromagnetic wave propagation through various media, we can begin to understand the available modes in a given system and how to couple light to these modes. In the following mathematical treatment of surface waves and SPPs, we will invoke Maxwell’s equations and leave out quantum mechanics, as the phenomena can be easily understood from a classical framework. Note, for simplicity, the media is always assumed to be isotropic, homogeneous, and having a magnetic permeability of $\mu = 1$.

1.3.1 Maxwell Wave Equation

First we will start with a variation of Maxwell’s equations in order to build the wave equations for p-polarized (transverse magnetic waves or TM) and s-polarized (transverse electric waves or TE) waves traveling through a media. From this, it will be evident that only TM waves can couple to surface plasmon polaritons. Note, the following derivation is an adaption from [Maier, 2004]16. Maxwell’s equations are as follows:

$$\nabla \cdot \vec{D} = \rho_{ext} \quad (1.1)$$
$$\nabla \cdot \vec{B} = 0 \quad (1.2)$$
$$\nabla \times \vec{E} = -\frac{\partial \vec{B}}{\partial t} \quad (1.3)$$
$$\nabla \times \vec{H} = \vec{J}_{ext} + \frac{\partial \vec{D}}{\partial t} \quad (1.4)$$

where $\vec{D}$ is the dielectric displacement, $\vec{B}$ is the magnetic induction or magnetic flux density, $\vec{E}$ is the electric field, $\vec{H}$ is the magnetic field, $\rho_{ext}$ is the external charge density, and $\vec{J}_{ext}$ is the external current density. In this particular derivation, we stray from tradition by including the external and internal charge and current densities for an explicit understanding of what drives the system (i.e external) and how the system (i.e. internal) responds. By taking the curl of Eq. 1.3 and Eq. 1.4 and combining them, we can derive the magnetic and electric field components of the wave equation. This yields:

$$\nabla \times (\nabla \times \vec{E}) = -\mu_0 \frac{\partial^2 \vec{D}}{\partial t^2} \quad (1.5)$$
Figure 1.2 Illustration of a dielectric-metal interface introducing the mathematical constructs coordinate system, propagation direction, and evanescent field profile.

using identities:

\[
\nabla \times (\nabla \times \vec{E}) = \nabla (\nabla \cdot \vec{E}) - \nabla^2 \vec{E} \quad (1.6)
\]

\[
\nabla \cdot (\varepsilon \vec{E}) \equiv \vec{E} \cdot \varepsilon + \varepsilon \nabla \cdot \vec{E} \quad (1.7)
\]

one can easily arrive at:

\[
\nabla (\frac{1}{\varepsilon} \vec{E} \cdot \nabla \varepsilon) - \nabla^2 \vec{E} = -\mu_0 \varepsilon_0 \varepsilon \frac{\partial^2 \vec{E}}{\partial t^2} \quad (1.8)
\]

Now assuming that \( \varepsilon = \varepsilon(r) \) is constant on the order of 1 optical wavelength, Eq. 1.8 collapses to:

\[
-\nabla^2 \vec{E} = -\mu_0 \varepsilon_0 \varepsilon \frac{\partial^2 \vec{E}}{\partial t^2} \quad (1.9)
\]

substituting in \( c = \frac{1}{\sqrt{\varepsilon \mu_0}} \):

\[
-\nabla^2 \vec{E} = -\frac{\varepsilon}{c^2} \frac{\partial^2 \vec{E}}{\partial t^2} \quad (1.10)
\]

To move any further, we have to make two assumptions about the electric field characteristics. The electric field has a harmonic time dependence and is propagating in the x-direction with an exponential decay (standard assumptions for a propagating wave), illustrated in Fig. 1.2. This is represented mathematically by the following:
\[ \vec{E} = \vec{E}(r, t) \] (1.11)

\[ = \vec{E}(x, y, z, t) \] (1.12)

\[ = \vec{E}(z)e^{-i\omega t}e^{ik_xx} \] (1.13)

Substituting Eq. 1.13 into Eq. 1.10, you arrive at:

\[ \frac{\partial^2 \vec{E}(z)}{\partial z^2} + (k_0^2\varepsilon - k_x^2)e = 0 \] (1.14)

where \( k_0 \) is the wave vector in vacuum and is equal to \( \omega/c \), \( k_x \) is the wave vector in the \( x \)-direction, and \( \omega \) is the angular frequency. Eq. 1.14 is the generic equation for a guided electromagnetic wave and is fundamental in describing electromagnetic fields and waves with respect to photonic devices. Furthermore, a parallel equation exists for the magnetic field which is perpendicular to the electric field.

To obtain the TM and TE wave equations describing the transverse magnetic and transverse electric field dynamics, Eq. 1.3 and Eq. 1.4 have to be solved resulting in explicit expressions for the field components. Continuing the derivation for the electric field, Eq. 1.3 in matrix form is:

\[
\begin{vmatrix}
\frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \\
e_x & e_y & e_z
\end{vmatrix} = \mu_0 \frac{\partial H_x}{\partial t} \hat{i} - \mu_0 \frac{\partial H_y}{\partial t} \hat{j} + \mu_0 \frac{\partial H_z}{\partial t} \hat{k}
\]

Performing the same procedure for the \( \vec{H} \) (i.e. Eq. 1.4) and equating the components results in:

\[ \frac{\partial H_x}{\partial y} - \frac{\partial H_y}{\partial z} = -i\omega\varepsilon_0\varepsilon e_x \] (1.15)

\[ \frac{\partial H_x}{\partial z} - \frac{\partial H_z}{\partial x} = -i\omega\varepsilon_0\varepsilon e_y \] (1.16)

\[ \frac{\partial H_y}{\partial x} - \frac{\partial H_x}{\partial y} = -i\omega\varepsilon_0\varepsilon e_z \] (1.17)

\[ \frac{\partial E_x}{\partial y} - \frac{\partial E_y}{\partial z} = i\omega\mu_0 H_x \] (1.18)

\[ \frac{\partial E_x}{\partial z} - \frac{\partial E_z}{\partial x} = i\omega\mu_0 H_y \] (1.19)

\[ \frac{\partial E_y}{\partial x} - \frac{\partial E_x}{\partial y} = i\omega\mu_0 H_z \] (1.20)
Using a Fourier transform to convert the partial derivative in the x-direction to wave vector domain \( \frac{\partial}{\partial x} = i k_x \) and including uniformity in the y-direction \( \frac{\partial}{\partial y} = 0 \), the previous set of equations collapse to:

\[
\begin{align*}
\frac{\partial H_y}{\partial z} &= -i \omega \varepsilon_0 \varepsilon E_x \\
\frac{\partial H_x}{\partial z} - i k_x H_z &= -i \omega \varepsilon_0 \varepsilon E_y \\
\frac{\partial E_y}{\partial z} &= i \omega \mu_0 H_x \\
\frac{\partial E_x}{\partial z} - i k_x E_z &= i \omega \mu_0 H_y
\end{align*}
\]

For the transverse magnetic waves, the only non-zero components will be \( \vec{E}_x \), \( \vec{E}_z \), and \( \vec{H}_y \) and for the transverse electric waves, the only non-zero components will be \( \vec{H}_x \), \( \vec{H}_z \), and \( \vec{E}_y \). To help visualize the concept of collapsing the previous equations, Fig. 1.3 illustrates the orientation of the electric field and magnetic field for TM (p-polarized) and TE (s-polarized).

**Figure 1.3** Illustration of a p-polarized and s-polarized light in terms of electric field and magnetic field components relative to incident plane and incident surface.
Following the previous discussion, the TM modes are described by:

\[
E_x = \frac{-i}{\omega \varepsilon \varepsilon_0} \frac{\partial H_y}{\partial z} \tag{1.27}
\]

\[
E_z = \frac{-k_x}{\omega \varepsilon \varepsilon_0} H_y \tag{1.28}
\]

and the corresponding wave equation for the TM mode is:

\[
\frac{\partial^2 H_y}{\partial z^2} + (k_0^2 \varepsilon - k_x^2) H_y = 0 \tag{1.29}
\]

The TE modes are described by:

\[
H_x = i \frac{\omega}{\varepsilon_0 \mu_0} \frac{\partial E_y}{\partial z} \tag{1.30}
\]

\[
H_z = \frac{-k_x}{\omega \mu_0} E_y \tag{1.31}
\]

and the corresponding wave equation for the TE mode is:

\[
\frac{\partial^2 E_y}{\partial z^2} + (k_0^2 \varepsilon - k_x^2) E_y = 0 \tag{1.32}
\]

With the previous polarized wave equations at our disposal, one can adequately understand wave propagation in vacuum where \( \varepsilon = 1 \). However, our goal is to properly described bound waves at a metal dielectric interface where surface plasmon polaritons exist. To do so, we need an accurate description of the media and how electromagnetic waves will interact with the media. For conducting metal oxides (i.e. the focus of this dissertation), we will evoke a dielectric function composed from a classical free electron gas model, also known as the Drude-Lorentz model (following section).

### 1.3.2 Dielectric Function of Free Electron Gas

The following section aims to mathematically characterize the response of electrons in the metal to an electric field. To articulate the power and simplicity of the following classical model, we will start with Newton's second law in deriving the electrons response to an AC electric field \( \vec{E}(t) \), of a TM wave.
\[ \vec{F} = m_0 \frac{\partial^2 x}{\partial t^2} = -e \vec{E}(t) \]  

(1.33)

where \( \vec{F} \) is the force exerted on a free electron, \( m_0 \) is the electron effective mass (also known as \( m^* \)), and \( e \) is the charge of an electron. Note, the far right side of Eq. 1.33 is the driving force of the AC electric field \( (i.e. \) incident TM wave). Moreover, Eq. 1.33 is the classical equation of motion for an electron in an oscillating electric field with no dampening. Practically speaking, electrons oscillating in a medium will experience dampening forces, such as Coulombic forces from electron-electron and ionized impurity-electron interactions. Incorporating this dampening term, Eq. 1.33 becomes

\[ m_0 \frac{\partial^2 x}{\partial t^2} + m_0 \gamma \frac{\partial x}{\partial t} = -e \vec{E}(t) \]  

(1.34)

where \( \gamma \) is the explicit dampening term defined as \( \gamma = e/\mu_e m_0 \) with \( \mu_e \) being the mobility of an electron. Eq. 1.34 is a well known differential equation with the solution \( \vec{x} = \vec{x}_0 e^{-i\omega t} \). Substituting the solution into Eq. 1.34 and assuming a harmonic time dependent (as in the previous section) driving electric field, we arrive at

\[ \vec{x} = \frac{e \vec{E}(t)}{m_0(\omega^2 + i\gamma \omega)} \]  

(1.35)

As a function of time, the electrons will undergo a displacement due the driving electric field, \( \vec{E}(t) \), governed by Eq. 1.35. Therefore, there will be a net electron polarization, \( \vec{P} \). The polarization of an electron gas is equal to \(-ne \vec{x}\), where \( n \) is the electron carrier concentration. The dielectric displacement, \( \vec{D} \), is linked to the polarization and electric field by

\[ \vec{D} = \epsilon_0 \vec{E} + \vec{P} \]  

(1.36)

\[ = \epsilon_0 \vec{E} - \frac{-ne^2 \vec{E}(t)}{m_0(\omega^2 + i\gamma \omega)} \]  

(1.37)

Furthermore,

\[ \vec{D} = \epsilon_0 \epsilon \vec{E} \]  

(1.38)

Solving for \( \epsilon \) using Eq. 1.38 results in
\[ \epsilon = 1 - \frac{n e^2}{\epsilon_0 m_0} \frac{1}{\omega^2 + i \gamma \omega} \]  

(1.39)

which can also be written as

\[ \epsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i \gamma \omega} \]  

(1.40)

with

\[ \omega_p = \sqrt{\frac{n e^2}{\epsilon_0 m_0}} \]  

(1.41)

where \( \omega_p \) is the plasma frequency, which corresponds to the resonant frequency of the entire electron gas. Since we are operating at frequencies below the plasma frequency (i.e. the regime where the metal has metallic character), we have to take into account the background polarization of the positive ionic cores, \( \tilde{P}_\infty = \epsilon_0 (\epsilon_\infty - 1) \). Eq. 1.40 now becomes

\[ \epsilon(\omega) = \epsilon_\infty - \frac{\omega_p^2}{\omega^2 + i \gamma \omega} \]  

(1.42)

where \( \epsilon_\infty \) is the high frequency dielectric constant, which typically ranges from 1 (vacuum) to 10 depending on the dielectric properties of the medium. Eq. 1.42 is the complex dielectric function, also known as the Drude model. This equation is essential in describing the response to a propagating (or driving) electromagnetic wave. More generally speaking, the complex dielectric function captures the electronic response to electric fields.

At this point, we have the necessary mathematical constructs to from the dispersion relationship for surface plasmon polaritons. In section 1.3.1, the equations governing TM and TE modes alongside the components of the propagating electromagnetic wave were formulated giving the wave characteristics. In section 1.3.2, the complex dielectric function was derived starting with Newton’s second law in a classical framework providing the materials response to an electromagnetic wave. Now we are in a position to constrain the modes along an interface via boundary conditions allowing for a further understanding of surface plasmon polaritons and other available modes in the our standard configuration.
1.3.3 Dispersion Relationship for Surface Plasmon Polariton

Practically speaking, it is beneficial to grow thin films that support surface plasmon polaritons, and other polaritonic modes, on transparent insulating or semi-insulating substrates for two reasons. First, ensuring transparency of the substrate in the coupling range of interest is of keen importance. For the Kretschmann configuration, which will be discussed in detail, light has to pass through a high index media, i.e. the substrate, to achieve a shift in momentum space allowing for coupling to these bound surface plasmon polaritons. Thus, the substrate has to be transparent in the spectrum of interest, otherwise coupling cannot occur. Secondly, it is advantageous for the substrate to be an insulator for the characterization of the electronic properties, such as carrier concentration and electron mobility. With that in mind, the standard configuration will be a three layer system: a metal surround by two dielectrics (air and substrate) as seen in Fig. 1.4

In the following derivations, we will consider two different scenarios. The first scenario is when the thickness \( d \) is infinitely large such that we are investigating one interface at \( z = 0 \). The second case is when \( d \) begins to approach the skin depth of the metal, which will give rise to coupled modes. For the first scenario, we will make three assumptions:

1. Metal has metallic character \( \equiv \text{Re}[\epsilon_{metal}] < 0 \), which corresponds to \( \omega \leq \omega_p \)
2. Propagation is in the x-direction \( \therefore H_y \text{ and } E_y \propto e^{ik_x x} \)
3. Propagating waves are confined to the interface with evanescent decay in the z-direction, i.e. continuity \( \therefore H_y \text{ and } E_y \propto e^{k_z |z|} \)

where \( k_z \) is the wave vector in the z-direction. Note, \( k_z \)'s reciprocal value is \( 1/\hat{z} \) which defines

![Figure 1.4 Illustration of a dielectric-metal-dielectric system, by which boundary conditions will be applied to derive the dispersion relationship for surface plasmon polaritons. The system is centered about the middle of the metal, where the thickness is d.](image-url)
the evanescent decay of the plasmon polariton in the z-direction. In the following discussion, we will identify TM modes first, followed by TE modes as they are the orthogonal complement. In identifying the TM modes, we will start by constructing a magnetic field, Eq. 1.43, oscillating in the y-direction, traveling in the x-direction (first exponential), and exponentially decaying (second exponential) for both layers. For \( z > \frac{d}{2} \)

\[
H_y = A_3 e^{ik_x x} e^{-k_{z,3} z} \tag{1.43}
\]

and using Eq. 1.27 and Eq. 1.28

\[
E_x(z) = \frac{1}{\omega \varepsilon_0 \epsilon_3} k_{z,3} e^{ik_x x} e^{-k_{z,3} z} \tag{1.44}
\]

\[
E_z(z) = -A_1 \frac{k_x}{\omega \varepsilon_0 \epsilon_3} e^{ik_x x} e^{-k_{z,3} z} \tag{1.45}
\]

and the same process for \( z < +\frac{d}{2} \) yields

\[
H_y = A_1 e^{ik_x x} e^{k_{z,1} z} \tag{1.46}
\]

\[
E_x(z) = -iA_1 \frac{1}{\omega \varepsilon_0 \epsilon_1} k_{z,1} e^{ik_x x} e^{k_{z,1} z} \tag{1.47}
\]

\[
E_z(z) = -A_1 \frac{k_x}{\omega \varepsilon_0 \epsilon_1} e^{ik_x x} e^{k_{z,1} z} \tag{1.48}
\]

where \( i = 1,2,3 \) for \( A_i, k_{z,i}, \) and \( \epsilon_i \) indicate the respective layer (i.e. 1 is the metal and 2,3 are the dielectric layers). By Maxwell’s equations, continuity exists between Eq. 1.45 and Eq. 1.48 requiring \( A_1 = A_3 \) and

\[
\frac{k_3}{k_1} = -\frac{\epsilon_3}{\epsilon_1} \tag{1.49}
\]

Substituting \( H_y \) for both layers into the TM wave equation, Eq. 1.29, we arrive at

\[
k_{z,1}^2 = k_x^2 - k_0^2 \epsilon_1 \tag{1.50}
\]

\[
k_{z,3}^2 = k_x^2 - k_0^2 \epsilon_3 \tag{1.51}
\]

Finally, by combining equations Eq. 1.49, Eq. 1.50, and Eq. 1.51 we arrive at the dispersion
Figure 1.5 Simulation of the dispersion relationship formulated at the interface between a dielectric and Drude metal. \( \omega \) is the angular frequency and \( k_x \) is the wave vector in the x-direction. Plotted is the real (left) and imaginary (right) components of the dispersion relationship.

relationship for a surface plasmon polariton bound to the interface between a dielectric and metal:

\[
K_{sp} = k_0 \sqrt{\frac{\epsilon_1 \epsilon_3}{\epsilon_1 + \epsilon_3}} \tag{1.52}
\]

Before discussing the characteristics of the dispersion relationship defined by Eq. 1.52, we need to identify the TE modes of the system as well. Following the same procedure as above and following continuity of \( E_z \), we arrive at

\[
A_1(k_1 + k_3) = 0 \tag{1.53}
\]

Recall in defining wave propagation characteristics, we confined the wave to the \( z = 0 \) interface. This requires the real component of the wave vector in the \( z \)-direction to be positive, thus for Eq. 1.53 to be valid \( A_1 = 0 \). Again, following continuity \( A_1 = A_3 = 0 \). In other words, all the field components for a TE mode are equal to zero, and TE modes do not exist for surface plasmon polaritons (assuming the magnetic permeability \( \mu \) is 1). Furthermore, the details of TE modes is an exercise left to the reader.

Eq. 1.52 is the dispersion relationship which describes the connection between the wave vector and angular frequency of the surface plasmon polariton. It can be seen from Eq. 1.52 that the dispersion is dependent on both the dielectric function of the metal and dielectric. The metals dielectric function can be simulated from the Drude model (Eq. 1.42) where the dielectric is typically non-dispersive, such as air (\( \epsilon \approx 1 \)). For completeness, Fig. 1.5 shows the real and imaginary compo-
Figure 1.6 Simulated real component of the dispersion relationship showing the trend of increasing carrier concentration.

ponents of the dispersion relationship for a metal-dielectric interface assuming a Drude metal. As the angular frequency is increased, the dispersion begins to approach the surface plasmon frequency, $\omega_{sp}$, with an increasing imaginary component. This is a direct result of the non-ideality of the metal, i.e. the metal is imperfect and slightly lossy. It can be seen as the angular frequency is increased past the surface plasmon frequency, we begin to enter a quasi-bound state which connects the surface plasmon polariton to the bulk plasmon polariton mode. Further increasing the frequency results in sustaining bulk plasmon polaritons, which are no longer bound modes. Note, bulk plasmon polaritons are radiative modes as they can be excited from free space. Ultimately, the dispersion characteristics can be tailored depending on the material properties.

The dielectric function of the metal is solely dependent on $\varepsilon_\infty$, $m_0$, $n$, and $\mu_0$; thus, the dispersion relationship is primarily built upon the aforementioned parameters (assuming the dielectric is non-dispersive). Moreover, the dispersion relationship can be tuned based on these parameters. For example, in a semiconductor setting (including CMOs) the key parameter that can be tuned is the carrier concentration $n$. A graphical representation of link between the carrier concentration and dispersion relationship is illustrated in Fig. 1.6. As the carrier concentration is increased from $2\times10^{20}$ cm$^{-3}$ to $5\times10^{20}$ cm$^{-3}$, the dispersion is shifted to higher frequencies. This effect is a direct result of increasing the plasma frequency $\omega_p$, which is proportional to $n$.

1.4 Plasmon Polariton Mode Thickness Dependence

Recall there are two scenarios for deriving the dispersion relationship of surface plasmon polaritons. We will now embark on the second scenario where the thickness $d$ is no longer considered to be infinite. In the case where the metal's thickness is below the skin depth, the bound interface modes can begin to "see" each other. In other words, the evanescent fields from the two interface modes can now interact, forming symmetric and asymmetric modes. Using the system illustrated in Fig. 1.4 and following the same general assumptions for the infinite thickness, we arrive at the following set of equations for TM modes:
For $z > d/2$

\[
H_y = Ae^{ik_x x} e^{-k_{z,3} z} \tag{1.54}
\]

\[
E_x(z) = iA \frac{1}{\omega \epsilon_0 \epsilon_3} k_3 e^{ik_x x} e^{k_{z,3} z} \tag{1.55}
\]

\[
E_z(z) = -A \frac{k_x}{\omega \epsilon_0 \epsilon_3} e^{ik_x x} e^{k_{z,3} z} \tag{1.56}
\]

and for $z < -d/2$

\[
H_y = Be^{ik_x x} e^{k_{z,2} z} \tag{1.57}
\]

\[
E_x(z) = -iB \frac{1}{\omega \epsilon_0 \epsilon_2} k_2 e^{ik_x x} e^{k_{z,2} z} \tag{1.58}
\]

\[
E_z(z) = -B \frac{k_x}{\omega \epsilon_0 \epsilon_2} e^{ik_x x} e^{k_{z,2} z} \tag{1.59}
\]

and for $-d/2 < z < d/2$

\[
H_y = C e^{ik_x x} e^{k_{z,1} z} + De^{ik_x x} e^{-k_{z,1} z} \tag{1.60}
\]

\[
E_x(z) = -iC \frac{1}{\omega \epsilon_0 \epsilon_1} k_{z,1} e^{ik_x x} e^{k_{z,1} z} + iD \frac{1}{\omega \epsilon_0 \epsilon_1} k_{z,1} e^{ik_x x} e^{-k_{z,1} z} \tag{1.61}
\]

\[
E_z(z) = C \frac{k_x}{\omega \epsilon_0 \epsilon_1} e^{ik_x x} e^{k_{z,1} z} + D \frac{k_x}{\omega \epsilon_0 \epsilon_1} e^{ik_x x} e^{-k_{z,1} z} \tag{1.62}
\]

Following Maxwell's equations, the electric field has to be continuous at both interfaces. Maintaining continuity requires, at $z = d/2$

\[
A e^{-k_{z,3} d/2} = C e^{k_{z,1} d/2} + D e^{-k_{z,1} d/2} \tag{1.63}
\]

\[
A \frac{k_{z,3} e^{-k_{z,3} d/2}}{\epsilon_3} = -C \frac{k_{z,1} e^{k_{z,1} d/2}}{\epsilon_1} + D \frac{k_{z,1} e^{-k_{z,1} d/2}}{\epsilon_1} \tag{1.64}
\]

and for $z = -d/2$

\[
B e^{-k_{z,2} d/2} = C e^{-k_{z,1} d/2} + D e^{k_{z,1} d/2} \tag{1.65}
\]

\[
B \frac{k_{z,2} e^{-k_{z,2} d/2}}{\epsilon_2} = -C \frac{k_{z,1} e^{-k_{z,1} d/2}}{\epsilon_1} + D \frac{k_{z,1} e^{k_{z,1} d/2}}{\epsilon_1} \tag{1.66}
\]
Furthermore, $H_y$ has to fulfill the TM wave equation in the three separate layers by the previous constraint

$$ k_{z,i}^2 = k_x^2 - k_0^2 \varepsilon_i $$

(1.67)

The previous system of linear equations can be solved resulting in an implicit dispersion relationship that characterizes the interaction of the two surface plasmon polaritons at each of the metal-dielectric interfaces.

$$ e^{-2k_1d} = \frac{k_{z,1}/\varepsilon_1 + k_{z,2}/\varepsilon_2}{k_{z,1}/\varepsilon_1 - k_{z,2}/\varepsilon_2} \frac{k_{z,1}/\varepsilon_1 + k_{z,3}/\varepsilon_3}{k_{z,1}/\varepsilon_1 - k_{z,3}/\varepsilon_3} $$

(1.68)

Unlike the dispersion relationship derived for the infinite thickness scenario, Eq. 1.68 has a thickness component, $d$, which stems from allowing two interface modes to be in close proximity. As a general rule of thumb, when the thickness is on the order of the incoming wavelength, the interfaces are far enough apart such that there are no coupled modes and Eq. 1.68 collapses to Eq. 1.52.

### 1.4.1 Surface Plasmon Polariton

Assuming the thickness of the metal to be finite results in a thickness component in the dispersion relationship, as seen in the previous section. Following Maxwell’s equations, a propagating electromagnetic wave will have an evanescent electric field decaying into both the dielectric and metal. When the metal’s thickness is decreased below the skin depth (defined as when the electric field in the z direction falls to 1/e), the two SPPs at each interface begin to couple. Coupling the modes results in a splitting of the original surface plasmon polariton mode into two distinguishable modes, which is described by Eq. 1.68. These modes are known as long range surface plasmon polaritons modes (LRSPP) and short range surface plasmon polaritons modes (SRSPP), where LRSPP is the upper branch and SRSPP is the lower branch, Fig. 1.7. For simplicity sake, the simulation of Eq. 1.68 in Fig. 1.7 assumes the dielectric claddings surrounding the metal are identical. The LRSPP and SRSPP modes have been studied over the past several decades, most notably by\textsuperscript{18,19,20,21}. Thus, the LRSPP and SRSPP modes have various labels throughout literature depending on the what characteristic the mode name is describing. For example, when mode splitting is being characterized by the electric field profiles, the modes are typically defined as asymmetric and symmetric, or in regard to the location on the dispersion plane, they are defined as $\omega_+$ or $\omega_-$ for being above or below $\omega_{sp}$. Henceforth, we will refer to the modes as LRSPP and SRSPP. Note, for the case where the dielectric claddings are not identical, the LRSPP mode will propagate at the interface with lower refractive
Figure 1.7 Modeled dispersion relationship as a function of thickness, d. As the thickness is decreased (c-d respectively), the dispersion splits into LRSPP and SRSPP where the upper branch begins to approach $\omega_p$, and the lower branch is further attenuated.

index (i.e. air) and the SRSPP will propagate at the higher refractive index interface (i.e. substrate). Each mode has unique characteristics as the thickness of the metal is decreased. For the SRSPP with decreasing thickness, the mode confinement increases as well as the attenuation of the mode. This mode attenuation can be seen by the SRSPP being shifted to lower $\omega$ values (i.e. Fig. 1.7 d). On the contrary, the LRSPP mode has decreasing mode confinement, increasing electric field confinement, and decreasing energy attenuation as the thickness is decreased. It can be seen from Fig. 1.7 (d) that upon further decreasing the thickness of the metal, the LRSPP mode begins to approach $\omega_p$, which is the onset of another plasmonic mode commonly referred to as the epsilon near-zero (ENZ) mode. This mode is discussed in the following subsection.

Considering the electric field profiles and charge distributions within the metal, one can begin to visualize the origins of these coupled modes. Fig. 1.8 illustrates the electric field profile and charge distribution in the three layered system for LRSPP's (left) and SRSPP's (right). Both modes have unique characteristics that define the respective mode. The LRSPP mode has an electric field that is symmetric about the center of the metal, still assuming that the surrounding dielectrics are
Figure 1.8 Evanescent field at both metal-dielectric interfaces (top) with corresponding charge distribution illustration (zoomed in, bottom). Colored arrows indicate charge motion while SPPs are excited.
identical. As the metal thickness is decreased, the electric fields present at each interface begin to overlap producing a larger confined electric field in the metal. The corresponding charge density is aligned with the electric field in the metal, as seen in the bottom illustration in Fig. 1.8(a). On the other hand, the SRSPP modes has an asymmetric evanescent electric field about the center of the metal, resulting in the charge distribution illustrated on the bottom of Fig. 1.8 (b). The two SPP’s propagating at each interface are 180° out of phase, giving rise to charge repulsion in each SPP. Thus, from a charge motion perspective, it’s easily seen that the SRSPP can be significantly dampened depending on the specifics of the system.

Given fixed electrical properties, that is carrier concentration, mobility, high frequency dielectric constant, etc, the thickness of the metal is the key parameter that dictates what modes will be present in the system. By the previous discussion, decreasing the thickness below the skin depth splits the mode into LRSPP’s and SRSPP’s. Furthermore, decreasing the thickness well below the skin depth of the metal (on the order of $\lambda/50$ where $\lambda$ is the wavelength of the exciting electromagnetic wave) forms another mode known as epsilon near zero or ENZ mode, which is an extension of the previous discussion.

1.4.2 Epsilon Near Zero Plasmon Polariton Mode

A relatively new class of materials, termed near zero media, have been attracting much attention for their unprecedented light matter interactions. Near zero media have one or more parameters, that is permeability or permittivity, near zero producing a unique electromagnetic response when probed. For the purpose of plasmon polaritons, the epsilon near zero (ENZ) mode, which is where the permittivity approaches zero, will be the focus of the following discussions.

The ENZ mode has received growing interest in the plasmonics community due to its revolutionary applications and fascinating phenomenon such as sub-wavelength diffraction, plasmonic waveguides, hyperbolic media, femtosecond polarization switching, nth order harmonic generation, etc. Most notably, ENZ modes have a near-zero group velocity and extremely high electric field confinement. Remembering that the group velocity, $v_g$, is defined as $\frac{\partial \omega}{\partial k}$, the flat dispersion seen in the illustration Fig. 1.9 (c) indicates that the group velocity tends to zero over a range $k_x$ values. Furthermore, this implies that the wave has a 'static-like' behavior and has ability to pass through distorted channels while exhibiting a zero phase advance. Consequently, wave guides comprised of ENZ materials have minimal limitations in regard to wave guide design.

As discussed in 1.3.2, in terms of plasmon polaritons, the dielectric function is detrimental in describing the wave characteristics. As such, the dielectric function (permittivity) tending to zero creates a unique opportunity to explore wave dynamics. A slight manipulation of Eq. 1.3 and Eq. 1.4 results in a classical representation of Maxwell’s equations, $\nabla \times \vec{E} = i\omega \mu \vec{H}$ and $\nabla \times \vec{H} = -i\omega \varepsilon \vec{E}$. By inspection, it is clear that $\varepsilon \approx 0$ (or $\mu \approx 0$) results in a decoupling of electricity and magnetism, given
Figure 1.9 Modeled dispersion relationship as a function of thickness, $d$. As the thickness is decreased (a-c respectively) to well below the skin depth, the dispersion splits further. Figure c shows the transition of the LRSPP to an ENZ mode and the significant attenuation of the SRSSPP. Figure d is an extended view of Figure c.

the appropriate frequency. From a fundamental perspective, this class of materials begin to open possibilities for unconventional light matter interactions.

Regarding the previous discussion of the plasmon polariton modes dependence on thickness, Fig. 1.9 illustrates the modes dispersion as the thickness of the conductor is decreased well below the skin depth (good rule of thumb is when $d<\lambda/50$). At this thickness, the LRSPP has transitioned to the ENZ mode where the dispersion is pushed to the plasma frequency and is practically dispersion-less over the range of accessible $k_x$ values. In addition, the SRSSPP has been further attenuated to lower $\omega$ values. Note, at high wave vectors $k_x$, the ENZ and SRSSPP both approach the surface plasmon frequency, $\omega_{sp}$, following the same trend as previously seen in the thicker case.

As expected, the electric field confinement in the ENZ layer is extremely high seen by the overlapping fields illustrated in Fig. 1.10 a) (top). Following the high electric field confinement, majority of the free carriers in the ENZ layer are participating in the plasmon oscillations. Thus, the ENZ mode can be conceptualized as a bound bulk plasmon polariton.
1.5 Coupling to Plasmon Polaritons

There are various geometries and methods for coupling to bound plasmon polaritons, such as grating coupling, prism coupling, highly focused optical beams, and near field excitation. For the purpose of this dissertation, we will focus on prism coupling schemes, i.e. the Kretschmann and Otto configurations. The Kretschmann and Otto configurations are some of the most widely used methods to observe surface plasmon polaritons, in addition to scanning near-field optical microscopy (SNOM) and grating coupling, dating back to the late 1960’s. In the Kretschmann configuration, a metallic film is directly deposited on a dielectric prism (such as CaF$_2$ or Al$_2$O$_3$). A beam of p-polarized light is transmitted through the prism and is incident on the metal-dielectric interface. At angles greater than the critical angle, total internal reflection is achieved. Upon achieving total internal reflection, an evanescent electric field is generated in the z direction with an in-plane momentum $k_x$ ($k_x = k_0 \sqrt{\varepsilon \sin \theta}$). The momentum shift in the incident $k_x$ due to increasing the incident angle is significant enough to match the surface plasmon polaritons $k_x$ resulting in coupling at the metal-air interface (Fig. 1.11a). This effect is also modeled in Fig. 1.12 (b) (red line). Note, the red line in Fig. 1.12 (b) is the light line or the dispersion relationship for light traveling through a medium and be tilted depending on the incident angle. The Otto configuration follows a similar concept with a minor alteration. A small gap is placed between the prism and metal film.
Total internal reflection is achieved at the prism-air interface, creating an evanescent field tunneling through air where the matching of $k_x$ takes place at the upper metal-air interface (Fig. 1.11b). The Otto configuration is usually used to probe the surface quality of a thin film. As the concepts behind coupling to the surface plasmon polaritons are identical, the Kretschmann configuration offers a more practical route.

In a typical thin film growth, a plasmonically active thin film is deposited on a dielectric substrate (typically single crystal Al₂O₃ or MgO). Therefore, a more complex Kretschmann configuration was used (Fig. 1.12 (a)). Following Fig. 1.12 (a), a CaF₂ prism is index matched to a dielectric substrate using an index matching fluid. As the p-polarized light passes through the prism-substrate interface, there is a slight change in direction following Snell's law. The subsequent process is identical to the original Kretschmann configuration. Note, in Fig. 1.12, the incoming p-polarized light is coupling to an ENZ mode. The configuration is unaltered to couple to this mode; however, the thickness of the metallic thin film is decreased to satisfy the ENZ condition in Eq. 1.68 (i.e. the upper branch of the split mode).

Experimentally, coupling will manifest itself as a minimum in the p-polarized reflected intensity as the incident angle is increased, seen in Fig. 1.12 (c). For simplicity, all reflectivity maps are modeled and measured as p-polarized/s-polarized light as only p-polarized light (or TM waves) couples to the mode of the system. In Fig. 1.12 (c), the black area indicates absorption and the white area indicates reflection of p-polarized light. Note, there are some limitations when coupling using the Kretschmann configuration. Since light is passing through the substrate to acquire the appropriate momentum shift, the transparency window of the substrate can limit the energy range of the light coupling in the system. In addition, at angles below the critical angle, there will not
Figure 1.12 a) Hybrid Kretschmann configuration illustrating the coupling of light to the ENZ mode used in experiments. b) Dispersion relationship of an ENZ mode and light line as a function of incident angle. c) Modeled reflectivity map for a thin film conductor on a dielectric substrate mimicking the hybrid Kretschmann configuration.
be total internal reflection (i.e. no evanescent wave). Therefore, coupling to the ENZ mode in this configuration cannot be achieved. This effect is seen by the dark band at approximately 45 degrees in the map in Fig. 1.12 (c).

1.6 Plasmon Polariton Applications

Now that we have a thorough understanding of different bound plasmon polariton modes and the coupling schemes used to access these modes, the following aims to provide a variety of current applications implementing plasmon polaritons.

1.6.1 Plasmon Sub-wavelength Waveguides

A central problem in the nano-photonics community is focusing light into nano-cavities when the wavelength of light is on the order of hundreds of nanometers or even microns depending on the spectrum of interest. Ultimately, the diffraction limit of light halts the ability to couple light to nanoscale devices. To circumvent these limitations, plasmon polaritons have been exploited due to their ability to confine light in areas less than $1/50^{th}$ of the incoming light. As such, plasmon polariton have enabled unprecedented waveguide capabilities.

One interesting study was performed by S. Bozhevolni et al., implementing channel plasmon

Figure 1.13 A plasmonic Y-splitter and Mach-Zehnder interferometer fabricated by S. Bozhevolni et al. where the top is SEM images, middle is AFM topological images, and bottom is scanning near-field optical microscope images.
polaritons (CPPs).\textsuperscript{13} CPPs are surface plasmon polaritons that are bound to the indented plasmonic material such as gold. The fundamentals are the same as previously discussed. The indentation in the metal film mimics a pseudo three layer structure (laterally) where there are two metal-dielectric interfaces brought close together. In this work, by milling V-shaped groves into a 1.8 $\mu$m gold thin film deposited on fused silica, the two metal-dielectric interfaces were fabricated. Applications of the CPPs include miniature bio-sensors and ultra compact plasmonic interconnects.\textsuperscript{13}

\subsection*{1.6.2 Plasmon Polariton Induced Hot Carrier Generation}

The need for higher efficiency photovoltaics is of paramount importance as current device schemes are limited. One possible solution is developing devices based on plasmon polariton induced hot carriers. There is an energy spectrum of hot electrons. For example, when a semiconductor is radiated with super-band gap light, the electrons in the valance band become "hot" enough (or have enough energy) to overcome the energy gap and are promoted to the conduction. Another example is intraband transitions, where the electrons in the conduction band absorb radiated light and are of a higher energy state. Furthermore, if the electrons absorb enough energy, they can be emitted through the photoelectric effect. As previously discussed, the extraordinary high electric field confinement exhibited by plasmon polariton coupling allows for unprecedented light matter interactions. Consequently, plasmonic structures can directly convert coupled light into electrical

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure14.png}
\caption{Hot carrier injection at a metal-semiconductor interface showing a) energy band diagram of hot carrier injection, b) illustration of device implementing hot carrier injection, and c) SEM micrograph of device. Image adapted from M.W. Knight \textit{et al.}\\}
\end{figure}
energy by generating hot electrons.\textsuperscript{28,29,30,31,12,32,27,33}

Recent investigations have shown hot electrons generated by plasmon polaritons can be used for light harvesting or detectors.\textsuperscript{27} Fig. 1.14 illustrates the concept of hot carriers being used in a detector device. M.W. Knight \textit{et al.} fabricated a metal-semiconductor interface with gold and n-type silicon, effectively creating a Schottky barrier (Fig. 1.14 a). By having small gold islands, the electric field confinement is enhanced allowing for an increase in hot electron energy. Upon achieving coupling between an incident photon (from a visible laser) and gold, hot carriers are generated where the electrons can overcome the Schottky barrier generating a photocurrent. Plasmon polariton based devices offer a unique approach to enhancing modern detectors and energy haverss.

### 1.6.3 Biosensing with Plasmon Polaritons

Surface plasmon polaritons have evanescent fields that extend far into the dielectric and are extremely sensitive to the surroundings. As such, changing the dielectric surrounding will change the energy at which coupling is achieved, following Eq. 1.68. Therefore, from a biomolecule detection perspective, surface plasmon polaritons are capable of detecting a variety of molecules. In fact, detecting various biomolecules is one of the most widely used application of surface plasmon polaritons.

A recent report from J. Feng \textit{et al.} demonstrates biomolecule detection using surface plasmon polariton generated on silver slit structures (Fig. 1.15a). By creating slits (or indentations), similar

![Figure 1.15](image-url.png)

**Figure 1.15** a) Illustrations showing biomolecules attached to a grooved silver thin film and b) changes in transmitted intensity and position as a function of glucose concentration (mg/dL). Image adapted from J. Feng \textit{et al.}\textsuperscript{34}
to the previous discussion for wave guiding, incident light can couple to the silver films. Note, Section 1.5 discussed coupling via Kretschmann and Otto configurations, but there are additional coupling schemes such as gratings or slits. In this particular case, the slits were engineering in such a way to from an interferometer seen in Fig. 1.15 b). Further, the silver slit structure was integrated with a microfluidic system where physiological concentrations of glucose in water were detected over a wavelength range of 400-800 nm. Fig. 1.15 b) demonstrates the devices detection capabilities. Changing the glucose concentration shifted the relative intensity by 40% confirming surface plasmon polariton based biosensors as a feasible alternative to current biosensors. 

As synthesis techniques for creating plasmonically active systems are made more accessible, a plethora of applications are beginning to arise. The previous discussions only cover a small number of applications. There are many others, such as surface plasmon polariton amplifiers and lasers, near-field nano-imaging and superlensing, etc.

### 1.7 Significance of Infrared Plasmonics

Despite the previously mentioned applications, plasmonics are yet to be established in the mid-IR. Over the past several decades, the plasmonics community has focused research in the UV, visible, and far-IR spectrum by exploiting noble metals, nitrides, and semiconductors because of the accessible carrier concentration-mobility combinations. Noble metals, such as gold and silver, have fixed carrier concentrations in the $10^{22}$ to $10^{23}$ cm$^{-3}$ range eliminating the possibility of infrared plasmonic applications. On the other hand, high mobility III-V semiconductors such as gallium arsenide (GaAs) and gallium nitride (GaN) can be doped to the $10^{17}$ to $10^{18}$ cm$^{-3}$ range with modest mobilities. At these carrier concentrations, the plasma frequency lies in the far-IR, illustrated in Fig. 1.16. In the $10^{19}$ to $10^{21}$ cm$^{-3}$ range, i.e. mid/near infrared regime, the mobility significantly drops to values on the order of 10 cm$^2$/Vs. With that said, a key parameter used in identifying the quality of a plasmonic material is the carrier mobility, and for the context of this dissertation electron mobility. Note, the plasmon polariton dampening coefficient, $\gamma$, is inversely proportional to the mobility; therefore, higher electron mobilities yield lower plasmon polariton dampening. Hence why modern semiconductors are bad mid-IR plasmonic materials. Fig. 1.16 illustrates the general trend of electron mobility, and plasma frequency, with carrier concentration (log-log scale). As the carrier concentration is increased, the plasma frequency exponentially increases following Eq. 1.41. In addition, the electron mobility steadily decreases, as previously discussed. The decrease in electron mobility can be attributed to additional electron scattering mechanisms, such as electron-electron scattering, electron-phonon scattering, impurity scattering, and defect scattering.

Although materials development for the mid-IR are lacking, there are interesting applications that motivate the materials search. In regards to biosensing, molecular vibrations can be found in the mid-IR. Thus there lies a desire to couple plasmon polaritons to molecular vibrations for sensing.
Figure 1.16 Electron mobility and plasma frequency as a function of carrier concentration where different colors indicate the corresponding spectral range where coupling is achieved.

capabilities. Further, modern IR detectors have to be constantly cooled with liquid nitrogen. With mid-IR plasmonics, uncooled IR detectors is a realization. Alongside detectors, mid-IR plasmonics could enable energy harvesters. There are enormous amounts of mid-IR energy released from heated objects from cars to the sun. Harvesting this wasted energy could have tremendous economical and environmental impacts.

1.8 Interest in Conducting Metal Oxides

Conducting metal oxides are a potential material system to fill the gap in mid-IR plasmonics due to their tunable carrier concentration in the $10^{19}$ to $10^{21}$ cm$^{-3}$ range while maintaining high mobilities. In the past decade, tin doped indium oxide (ITO) has been the most promising candidate with the highest reported mobilities in the range of 100 cm$^2$/Vs.$^{38,39,40,41}$ Fig. 1.17 plots the electron mobility as a function of carrier concentration for indium oxide doped with a variety of dopant’s including tin, zirconium, and titanium.$^{38}$ While the mobilities displayed in Fig. 1.17 are quite high for the $10^{19}$ to $10^{21}$ cm$^{-3}$ range, the resulting absorption full width half max (FWHM) values are on the order of 1000 cm$^{-1}$.4,42 In a variety of applications, such as IR detectors and biosensing, the FWHM max is
the limiting factor determining the resolution of the device. A promising high mobility candidate to replace doped indium oxide is doped cadmium oxide.

The first report of high mobility cadmium oxide was in 1969 by F.P. Koffyberg. In this report, cadmium oxide single crystals underwent annealing studies and temperature dependent electrical characterization providing effective mass, band gap, and defect concentration values. Most importantly, electron mobilities as high as 300 cm$^2$/Vs at room temperature were reported. Fast forward almost 50 years, E. Sachet et al. reports dysprosium doped cadmium oxide with mobilities as high as 500 cm$^2$/Vs in thin film form. With the use of density functional theory, high quality oxygen plasma assisted molecular beam epitaxy, and temperature dependent electrical measurements, they report an interesting observation with doped cadmium oxide. As the dysprosium concentration, well below 0.1%, was increased, a peak in mobility was observed. Cadmium oxide is intrinsically a n-type semiconductor due to oxygen vacancies. As such, as the dysprosium concentration was increased, a strong Moss-Burstein shift was observed where the Fermi level is pushed into the conduction band. Effectively, as the Fermi level is pushed higher in the conduction band, the formation energy of oxygen vacancies is pushed to higher energies; thus, decreasing the number of oxygen vacancies, which are the primary scattering centers (confirmed with DFT). Ultimately, the decrease in defects

Figure 1.17 Hall mobility as a function of hall electron concentration for indium oxide doped with tin, zirconium, titanium, and hydrogen. Image adapted from N. Preissler and O. Bierwagen.
provided the system with higher electron mobilities. The following chapters aim to build upon the aforementioned work to provide an understanding of the dopant role in doped cadmium oxide, and to explore the unprecedented plasmon polariton applications of doped cadmium oxide.
Experimental Details

The following are experimental details describing the deposition methods, post-processing techniques, and sample characterization for all studies discussed. All samples followed the same cleaning procedure before thin film deposition:

1. Sonicate in acetone for 10 minutes
2. Spin coat sample at approximately 4000 RPM and expose to acetone, isopropanol, and methanol for further sample cleaning
3. Expose sample to UV-Ozone for 10 minutes to mitigate residual hydroxides

2.1 Dual Radio Frequency Magnetron Co-sputtering

2.1.1 Dual RF System Geometry

The dual radio frequency (RF) co-sputtering system geometry is illustrated in Fig. 2.1. The sputtering chamber consists of a load lock, heated rotating manipulator, pressure gauges, and two water cooled 2” MeiVac MAK sputtering magnetrons. The load lock, connected to a roughing pump, was pumped to approximately 50 millitorr before sample transfer to facilitate a lower base pressure prior to deposition. A substrate, such as Al₂O₃, Si, Pt, MgO, or GaN, was transferred to the heated rotating manipulator for thin film growth. A Pfeiffer Balzer 170 L/s turbo-molecular pump (TMP) was connected to the sputtering chamber, which allowed for a clean base pressure in 10⁻⁸ Torr range. The Cd RF sputtering magnetron was positioned normal to the substrate and a dopant sputtering magnetron, such as Dy, Y, or In, was parallel to the substrate surface. Lastly, convectron gauges were used to monitor the deposition and load lock pressures, and an ion gauge was used to monitor the main chamber base pressure before deposition.
Figure 2.1 Chamber schematic of dual RF magnetron sputtering with Cd source positioned normal to the substrate and a dopant source positioned parallel to the substrate. The load lock (left sphere) serves as a staging platform for low pressure transfers. Note, transferring occurs from left to right.

### 2.1.2 Dual RF Deposition

Thin films of doped cadmium oxide were reactively deposited with 99.9999% pure metallic cadmium and a metallic dopant source. All films were sputtered in a 4:1 argon to ozone-oxygen environment at 100 millitorr. The power densities applied to the Cd and dopant source were 8 W/cm$^2$ and 2-14 W/cm$^2$, respectively. The RF plasmas were driven by an Advanced Energy RFX-600 sources and a Manitou Systems manual matching networks.

All films were grown on substrates bonded to a stainless steel puck using silver paste for thermal contact. In a typical deposition, the substrate surface was kept at 370°C and monitored by a Raytek 1.6 µm MM Series Pyrometer. During deposition, the substrates were rotated at 0.25 Hz to facilitate uniform depositions.

### 2.2 RF and Pulsed-DC Magnetron Co-sputtering

Thin films grown by RF and pulsed-DC magnetron co-sputtering utilize a relatively new regime of sputtering known as high-power impulse magnetron sputtering, or HiPIMS.
2.2.1 Pulsed-DC Magnetron Sputtering Introduction

Conventional magnetron sputtering plasmas are sustained by either DC or radio frequency (RF) power, which is typically chosen based on the target resistivity. In the past decade, deposition from pulsed DC plasmas have gained increasing attention due to their versatility and applications. Unlike DC and RF, pulsed DC plasmas are not limited to target resistivity. A variety of thin films have been deposited from oxide targets via pulsed DC, such as indium tin oxide (ITO)\textsuperscript{46} and aluminum doped zinc oxide (AZO)\textsuperscript{47}. In addition to target versatility, pulsed DC allows for a higher degree of control in regard to plasma dynamics. By changing the duty cycle and power density applied to the target, one can span the plasma densities and bombardment energies necessary for specific applications, e.g. high density and smooth films.

Using pulsed DC, one can vastly extend the power limitations typically imposed by target melting temperature or the magnetron depoling, provided the durations are short. For example, power densities on the order of 10 W/cm\textsuperscript{2} are used commonly to sputter materials like HfO\textsubscript{2}, In\textsubscript{1-x}Sn\textsubscript{x}O\textsubscript{3}, and TiN. This produces ionization fractions on the order of 10%. In many cases, a higher ionization fraction is desired, for example, to increase oxidation in a reactive deposition, or to promote additional energetic bombardment. If ionization fractions exceed 80% a self-sputter regime can be reached where the bombarding species is primarily the target material (i.e., gasless sputter-

![Diagram](image_url)

**Figure 2.2** Duty cycle vs peak power density bubble map defining sputtering regimes where pulsed DC, modulated pulsed power (MPP), and high-power impulsed magnetron sputtering are achieved. The dashed line indicates the DC sputter limit, or target damage threshold. Image adapted from J. Gudmundsson\textsuperscript{45}.

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ing\textsuperscript{48}. The power densities needed to access this ionization extreme would overheat conventional cathodes if run continuously. They can, however, be sustained when operated in pulsed mode. Fig. 2.2 represents the maximum peak power density achievable given a fixed duty cycle before target damage occurs. Imposing a duty cycle where the on time is 5-10\% and pulse duration is on the order of 100 $\mu$s achieves this condition. During these short pulses, power densities $\geq$ kW/cm$^2$ can be achieved, leading to high sputter rates, advantageous substrate bombardment, high reactivity, denser as-deposited films, and a reduced surface roughness\textsuperscript{45}. This regime of pulsed DC sputtering is known as high-power impulse magnetron sputtering (HiPIMS). Note, throughout literature, the different regimes of pulsed DC have various labels depending on the peak power density, peak current, voltage characteristics, and ionization fractions. With that in mind, HiPIMS is typically labeled as modulated pulsed power, high-power impulse magnetron sputtering, high power pulsed magnetron sputtering, and pulsed DC.\textsuperscript{45,49}

### 2.2.2 System Geometry

The RF and pulsed-DC magnetron co-sputter system geometry is illustrated in Fig. 2.3. The sputtering chamber schematic follows the aforementioned dual RF geometry with 2 exceptions, sputtering magnetron orientation and plasma driver. The two 2” MeiVac MAC sputtering sources were oriented approximately 45\° relative to the manipulator (i.e., substrate) normal. In addition, the pulsed-DC cadmium plasma was driven by a Starfire Industries Impulse Pulsed Power Module and an Advanced Energy MDX 1.5K DC power supply.

### 2.2.3 Deposition

Heteroepitaxial thin films of doped cadmium oxide were reactively deposited with 99.9999\% pure metallic cadmium and a metallic dopant source. All films were sputtered in an argon-oxygen environment at 10 millitorr flowing 19 sccm Ar and 13 sccm O$_2$. The HiPIMS parameters were 800 Hz and 80 $\mu$s pulse time, producing a 1250 $\mu$s and 6.4\% duty cycle. The DC power supply that feed the HiPIMS unit was set in constant voltage mode at 400V. To modulate the dopant concentration, the power density and substrate-to-target distance of the dopant source were varied from 2-14 W/cm$^2$ and 4-20 cm, respectively. Furthermore, the RF plasma was driven by an Advanced Energy RFX-600 source and a Manitou Systems manual matching network.

All films were grown on substrates bonded to a stainless steel puck using silver paste for thermal contact. The substrate surface was kept at 370\°C and monitored by a Raytek 1.6 $\mu$m MM Series Pyrometer. During deposition, the substrates were rotated at 0.25 Hz to facilitate uniform depositions.
2.3 Post Deposition Process

2.3.1 High Temperature Furnace Anneal

Post deposition, all samples were annealed in an isolated tube furnace at 700°C in O₂ for approximately 30 minutes. Note, some exceptions apply. For example, extremely thin films (less than 10 nm) and films grown on substrates with a large lattice mismatch were annealed at 600°C to mitigate film deterioration (island formation and evaporation).

2.3.2 Sample Characterization Preparation

For Hall effect measurements, samples underwent a weak HCl acid etch to form contact pads for the Van der Pauw method. Semiconductor wafer dicing tape (polyethylene) was used as template for the etch to reduce residual contaminates on the surface post-processing. After placing a 1 cm² polyethylene pad on the thin film surface, 10% HCl was used to etch or dissolve the film leaving behind a 1 cm² pad for reproducible Hall effect measurements.
2.4 Sample Characterization

The sample characterization techniques in the following subsections were performed at North Carolina State University. Techniques used at other facilities and universities will be discussed as it becomes relevant.

2.4.1 X-ray Diffraction

X-ray diffraction experiments were carried out using a Panalytical Empyrean diffractometer with several different optics options. To identify crystal orientation and phase, a Bragg-Brentano geometry was used employing a Pixel 2-D area detector and a programmable divergence slit incident beam optic. For single crystal and epitaxial thin film characterization, a parallel plate collimator (0.18°) with a Xe-proportional counter detector and a Ge double bounce hybrid monochromatic incident beam were used. All data analysis was carried out using Panalytical's High Score Plus software.

2.4.2 X-ray Reflectivity

X-ray reflectivity (XRR) measurements were performed using a Panalytical Empyrean diffractometer in a glancing angle geometry with a parallel plate collimator (0.18°) Xe-proportional counter detector and a Ge double bounce hybrid monochromatic incident beam. To mitigate divergence, a 1/32 slit was used on the incident optics. All XRR data was fitted using Panalytical's X’pert Reflectivity software, giving roughness, thickness, and density information.

2.4.3 Electrical Characterization

Electrical transport properties were characterized using an Ecopia HMS-3000 Hall measurement system. Electrical contact was made on the corners of the sample's 1 cm$^2$ pad using gold coated probes, also known as the Van der Pauw method. To measure the Hall voltage, where the transport properties can be derived, a current of 10 mA was used under a 0.51 T magnetic field.

2.4.4 Atomic Force Microscopy

Surface morphology was characterized using an Asylum Research MFP-3D atomic force microscope (AFM) in tapping mode, recording the height and phase signals. Aspire aluminum coated silicon conical AFM tips with a spring constant and resonant frequency of 40 N/m and 300 kHz, respectively, were used to probe the surface.
2.4.5 Optical Characterization

Optical studies were carried out using a J.A. Woollam IR-VASE ellipsometer in reflectivity mode. To measure plasmon polariton resonance in the Kretschmann configuration, a custom aluminum stage was built to house the sample and CaF$_2$ prism (courtesy of Dr. Edward Sachet). This stage was then mounted on the IR-VASE using a Thorlabs PM4/M prism holder. Note, to ensure optical contact between the CaF$_2$ prism and sample, Cargille Series M 1.720 index matching fluid was used. Refer to Chapter 1 for sample orientation illustrations.

2.5 Transfer Matrix Simulations

To simulate the optical response of various plasmonic modes, a transfer matrix method was employed. The simulation was built modeling the Kretschmann configuration multilayer system with a dispersive 90° CaF$_2$ prism, sapphire substrate, Drude metal (single and multilayer), and air configuration (Fig. 1.12). Following Z. Knittl’s "Optics of Thin Films", the transfer matrix, referred to as the system transfer matrix, builds upon Fresnel equations and Maxwell equations to construct the aforementioned modeled reflectivity maps. By infinitely summing all possibly reflections and refractions (Fresnel) over multiple interfaces and assuming electric field continuity across each interface (Maxwell), a system matrix can be formed where the total reflection and refraction can be calculated. Note, to simplify the transfer matrix, a reduced matrix was implemented to calculate only reflection. The modeling Matlab code can be found in the Appendix.

With such an effective simulation tool at our disposal, it is worthwhile to discuss how the properties of the Drude metal (i.e. doped cadmium oxide) affect the plasmon polariton absorption features. As discussed in Chapter 1, several characteristic parameters determine the absorption shape (which is related to the dispersion relationship) and behavior of plasmon polariton mode, such as effective electron mass, high frequency dielectric constant, carrier concentration, mobility, and thickness. However, some variables cause similar perturbations to the absorption spectra due to the convoluted variable dependence. The following figures illustrate a systematic variation of said variables. Note, except for the parameter being varied, the values used in the dielectric function calculation for the Drude metal are similar to a typical doped cadmium oxide thin film-0.20 effective electron mass, 5.5 high frequency dielectric constant, 40 nm thickness, $2.5 \times 10^{20}$ cm$^{-3}$ carrier concentration, and 250 cm$^2$/Vs electron mobility.

Fig. 2.4 a) depicts the coupling of light to a surface plasmon polariton with a thickness on the order of the skin depth. The reflectivity map is similar to the dispersion relationship- as the energy and incident angle (or $k_x$) of the incoming p-polarized light is increased, the coupling follows a logarithmic shape approaching the $\omega_{sp}$. As the thickness is decreased (b-c), the surface plasmon polariton splits into the SRSPP and LRSPP. With both modes (SRSPP and LRSPP) available in a given
system, only weakly coupling occurs at low angles (or k\textsubscript{x} values). At higher angles, the two modes converge, which is accurately captured in the previous dispersion plot, Fig. 1.9 d). As the thickness is further decreased approaching \( \lambda/50 \), the ENZ mode can be observed. Over the entire range of angles, the coupling is relatively flat and non-dispersive, following Fig. 1.9 c). Note, the following will be aimed at understanding parameter variations solely in the ENZ mode as the same principles can be extended to the SPP mode.

The plasma frequency, Eq. 1.41, is proportional to the carrier concentration and inversely proportional to the effective mass and higher frequency dielectric constant. Thus, as these values increase or decrease, a shift in the plasma frequency will occur. Keeping this in mind, Fig. 2.5 shows the ENZ mode absorption as a function of effective electron mass. As the effective electron mass, \( m^* \) or \( m_0 \), is decreased, the plasma frequency is shifted to higher energies as expected. In addition, the absorption FWHM is significantly broadened.

Fig. 2.6 shows the ENZ mode absorption as a function of high frequency dielectric constant. As the high frequency dielectric constant is decreased, the plasma frequency is shifted to higher energies as expected. Additionally, the absorption at higher angles resembles that of Fig. 2.4 c), indicating the decrease in electron screening has changed the thickness requirements to sustain a single ENZ mode forming the split mode nature discussed in Chapter 1.

Fig. 2.7 shows the ENZ mode absorption as a function of electron carrier concentration. Increasing the carrier concentration results in a strong shift in the plasma frequency, which is a fundamental observation for plasmon polaritons. Again, the change in absorption percentage is due to the skin depth of the Drude layer (or metal) changing. As the skin depth of the Drude layer changes, the required thickness to achieve total absorption has changed, \textit{i.e.} for lower carrier concentrations the conductor needs to be thicker.

Lastly, Fig. 2.8 shows the ENZ mode absorption as a function of electron mobility. Decreasing the mobility results in significant broadening while the plasma frequency remains constant. As the mobility is only inversely proportional to the plasmon dampening, only the width of the absorption is expected to change.

The previous modeled dispersion relationships using Eq. 1.68 accurately captures the modes of the system and is useful for understanding the development of different plasmon polariton modes. However, it does not take into account several realistic parameters such as the critical angle, substrate transparency, dissimilar dielectric claddings, dispersion line brocading, etc. As seen by the previous discussion, transfer matrix simulations accurately capture these parameters and offers the additional advantage of constructing multilayer structures. Hence, for modeling experimental results, the transfer matrix is superior.
Figure 2.4 Simulated transfer matrix reflectivity map showing the absorption profile as thickness is decreased from 300 nm to 40 nm (a-d respectively) in a typical doped cadmium oxide system. Figures a) and d) are the surface plasmon polariton and ENZ mode respectively. Figures b) and c) capture the splitting of the mode. Note, reflectivity is plotted as p-polarized/s-polarized.
Figure 2.5 Transfer matrix simulation of electron effective mass decreasing from 0.4 to 0.1 in a typical doped cadmium oxide thin film system.
Figure 2.6 Transfer matrix simulation of high frequency dielectric constant decreasing from 7.0 to 2.5 in a typical doped cadmium oxide thin film system.
Figure 2.7 Transfer matrix simulation of electron concentration, or carrier concentration, decreasing from $4.0 \times 10^{20} \text{ cm}^{-3}$ to $8.0 \times 10^{19} \text{ cm}^{-3}$ using the electrical properties of a typical doped cadmium oxide system.
Figure 2.8 Transfer matrix simulation of electron mobility decreasing from 500 cm$^2$/Vs to 50 cm$^2$/Vs in a typical doped cadmium oxide system.
Chapter 3

Doped Cadmium Oxide Thin Films

Originally, the doped cadmium oxide work done at North Carolina State University was performed by Dr. Edward Sachet. Dysprosium doped cadmium oxide was grown epitaxially on magnesium oxide substrates via molecular beam epitaxy (MBE) offering unprecedented mobilities as high as 500 cm$^2$/Vs. The investigation into the high mobility of dysprosium doped cadmium oxide resulted in the understanding of a unique oxide system, which is discussed in detail in the following sections. While doped cadmium oxide synthesized via MBE offers a unique advantage to establish the relationships between defect chemistry, composition, and electrical properties, the complexities associated with MBE present barriers for future applications. For example, the extremely low growth rates, complex user training, and financially exhaustive nature limit the throughput and ultimately the ability to characterize and study the material in a fast dynamic environment. As such, there exists a need to develop additional synthesis techniques that are a feasible alternative to MBE. Thus, we propose two techniques- reactive dual radio frequency (RF) magnetron sputtering and reactive pulsed-direct current (DC) magnetron co-sputtering.

3.1 Dual RF Magnetron Sputtering

RF magnetron sputtering offers many attractive features such as high throughput, high uniform coverage, and low-cost equipment. In addition, unlike MBE, RF sputtering allows for a diverse range of materials to be accessed (e.g. ZnO$^{51}$, TiO$_2$$^{52}$, Zn$_3$N$_2$$^{53}$, and c-BN$^{54}$) with a variety of desirable properties. In regards to doping CdO, sputtering opens the possibility for a vast number of dopants to be explored. The following studies identify several dopants for the CdO system, and the resulting electrical and structural properties.

The experimental design and parameters for synthesizing doped cadmium oxide via dual RF magnetron sputtering can be found in Chapter 2.
3.1.1 Dysprosium Doped Cadmium Oxide

For a direct comparison to MBE, the first dopant used in the dual RF magnetron sputtering of
doped cadmium oxide was dysprosium. By doping with dysprosium and examining the electrical
and structural properties, one can accurately identify if dual RF magnetron sputtering is a feasible
alternative to MBE for this specific oxide system.

![Graph showing mobility as a function of carrier concentration for dysprosium doped cadmium oxide](image)

**Figure 3.1** Left: Mobility as a function of carrier concentration for dysprosium doped cadmium oxide (red diamonds) beginning with intrinsic cadmium oxide labeled intrinsic. Lines connect data points in order of increasing dopant concentration beginning at intrinsic. Right: Cadmium oxide rocksalt structure with a dysprosium atom (gray atom) substitutionally placed on a cadmium site.

Fig. 3.1 (left) shows the electrical properties of dysprosium doped cadmium oxide (Dy:CdO)
starting with intrinsic, or no doping. Note in Fig. 3.1 (left), the lines connect the data points in order
of increasing dopant concentration starting at intrinsic CdO. Upon initially doping, two features
can be observed - a reproducible decrease in carrier concentration and a sharp rise in mobility.
We believe this initial decrease in carrier concentration can be explained from a Gibbs energy of
formation perspective. At room temperature, the energy of formation for CdO is approximately -520
kJ/mol, while for Dy₂O₃ is -1771 kJ/mol.⁵⁵,⁵⁶ Therefore, introducing dysprosium into the cadmium
oxide lattice will increase the propensity for oxidation, decreasing the number of oxygen vacancies
which are the primary source of n-type carriers and scattering centers (that is decrease the carrier
concentration and increase the mobility).

It is worth discussing the mechanisms by which the decrease in carrier concentration occurs
as it will be useful for future discussions. Dy has a stable ²⁺ oxidation state allowing for a neutral
charge when 'placed' on a Cd site. In this case, the ²⁺ oxidation state facilitates a decrease in oxygen
vacancies (due to the large negative energy of formation) without adding electrons to the conduction band. Another possible mechanism is that Dy$^{3+}$ is healing oxygen vacancies faster than adding additional electrons to the conduction band (only at these initial doping conditions). In other words, if at low dopant concentrations the Dy atom ratio to oxygen vacancy reduction is 1:1, every Dy will effectively decrease the carrier concentration by one electron. Further investigation of Dy:CdO will shed light on the mechanism responsible for the observed initial decrease in carrier concentration.

As the dysprosium concentration is increased further, a sharp rise in carrier concentration and mobility can be observed. This characteristic feature was first observed by Sachet et al. and introduced in 1.8. Essentially, the large Moss-Burstein shift increases the formation of oxygen vacancies causing a reduction in scattering centers, ultimately enabling a higher mobility semiconductor. At elevated dopant concentrations, a precipitous drop in mobility can be observed. DFT calculations have shown for Dy:CdO at higher carrier concentrations, compensating defects, primarily cadmium vacancies, arise ultimately decreasing the mobility.\textsuperscript{57}

From an electronic properties perspective, dual RF magnetron sputtering displays a similar peak in mobility compared to MBE. It’s worth noting that these films were grown on c-plane sapphire, while the MBE films were grown epitaxially on lattice matched magnesium oxide (MgO). With that said, films grown on MgO will intrinsically have a higher mobility due to less scattering mechanisms. Nevertheless, both growth techniques exhibit excellent electrical properties.

To examine the crystal quality, Fig. 3.2 shows X-ray diffraction data for Dy:CdO grown via RF
sputtering. For CdO growth on c-plane sapphire, the preferred crystallographic registry occurs when the (001) plane of CdO is tilted by 23.5° relative to sapphire (00.1) with a tilt direction parallel to sapphire <10.0>. Thus, when aligned to the thin film surface, only the (00.6) sapphire peak satisfies diffraction conditions (black curve Fig. 3.2 left). Tilting off axis and aligning to the (111) peak, one can observe a single diffraction peak indicating a single growth orientation (red curve Fig. 3.2 left). To complement the 2Theta diffraction data, a (111) phi scan is shown in Fig. 3.2 (right). As previously reported, CdO has an in-plane alignment of [100]||[01.0] producing three individual CdO orientations spaced by 120 deg. The 2Theta data in conjunction with (111) phi satisfies the criteria of epitaxial growth.

The aforementioned electrical and structural properties confirm RF sputtering as a feasible synthesis alternative to MBE for the doped cadmium oxide system. Now, with the assistance of dual RF magnetron sputtering, the relationships between dopant, and electrical and structural properties can be explored.

### 3.1.2 Aluminum Doped Cadmium Oxide

Aluminum doped cadmium oxide (Al:CdO) has been synthesized by various methods including spray pyrolysis, sol-gel, RF sputtering, and pulsed laser deposition (PLD). In addition, reports of Al:CdO have large discrepancies in the electrical and structural properties; thus, we aim to provide additional information to fully understand the role of aluminum in the cadmium oxide lattice. Following Fig. 3.3 (right), aluminum's ionic radius is small enough that it can occupy both interstitials and cadmium sites. When six-coordinated, aluminum has an ionic radius 0.535 Å which is significant for two reasons— it can fit in interstitial positions and grain boundary regions, and it is 56% different from cadmium. When occupying interstitial positions or grain boundary regions, aluminum's 3+ oxidation state will be compensated by adding three electrons to the conduction band. Alternatively, if aluminum substitutionally occupies a cadmium site, one electron will added to the conduction band, illustrated by the following Kroger-Vink notation:

$$
\text{Al}_2\text{O}_3 \xrightarrow{\text{CdO}} \text{2Al}^{3+}_{\text{Cd}} + \text{2O}_\text{δ}^+ + \text{2n} + \frac{1}{2} \text{O}_2(g)
$$

(3.1)

Ultimately, at higher aluminum concentrations, significant lattice distortions will occur due to the large ionic radius mismatch. Moreover, additional orientations should be observable via XRD caused by compensating the large ionic radius mismatch.

Fig. 3.3 (left) shows mobility as a function of carrier concentration for Al:CdO grown on c-sapphire. At small dopant concentrations, the mobility is constant at approximately 290 cm²/Vs while the carrier concentration is steadily increasing from $1.5\times10^{19}$ cm⁻³ to $4.4\times10^{19}$ cm⁻³. The constant mobility with increasing carrier concentration indicates $\text{Al}^{3+}$ is an effective n-type dopant,
and induces additional scattering mechanisms. From the previous discussion, increasing the carrier concentration shifts the Fermi level to higher energies producing higher vacancy formation energies resulting in an increase in mobility. The constant mobility seen with aluminum suggests there are competing mechanisms, such as decreasing vacancies from the Fermi level shift while increasing vacancies due to structural defects. At carrier concentrations higher than $6.5 \times 10^{19}$ cm$^{-3}$, the mobility continuously decreases from 271 to 133 cm$^2$/Vs suggesting the mobility is limited by defects within the crystal. Supporting XRD data is shown in Fig. 3.4. The bottom black two-theta-omega scan is for intrinsic CdO aligned to the thin film surface. As previously discussed, due to the unique growth on c-plane sapphire, only the sapphire diffraction peaks are observable. As the aluminum concentration is increased, additional orientations can be observed, indicating a polycrystalline thin film. Note from XRD, no Al$_2$O$_3$ or additional phases were detected at all concentration ranges.

Aluminum doped thin films grown via dual RF magnetron sputtering on c-sapphire prove aluminum to be an effective n-type dopant. However, due to the significant ionic radius mismatch between aluminum and cadmium (or strain associated with interstitials), significant lattice distortion occurs resulting in a continuous decrease in mobility.
Figure 3.4 Bragg-Brentano X-ray diffraction data for aluminum doped cadmium oxide starting with intrinsic (bottom) and increasing aluminum content (upward). Asterisk denotes c-plane sapphire substrate diffraction peak.
3.1.3 Yttrium Doped Cadmium Oxide

To further investigate the role of ionic radius and electronic configuration, we propose yttrium as another dopant for the cadmium oxide system. The ionic radius of six coordinated Y$^{3+}$ is 0.90 Å, which is only 5% different than Cd$^{2+}$; thus, minimal perturbations to the crystal lattice will occur (Fig. 3.5 right). Additionally, Y’s most stable oxidation state is 3$. Therefore, we suspect Y:CdO will yield similar electronic and structural properties to that of Dy:CdO.

Few reports exist for yttrium doped cadmium oxide (Y:CdO). In these reports, techniques such as metal organic chemical vapor deposition (MOCVD)$^{63}$ and ultrasonic spray pyrolysis$^{64}$ we exploited. However, to the best of our knowledge, sputtering has not been employed for yttrium doping cadmium oxide.

![Figure 3.5](image.png)

**Figure 3.5** Left: Mobility as a function of carrier concentration for yttrium doped cadmium oxide beginning with intrinsic cadmium oxide, labeled intrinsic. Lines connect data points in order of increasing dopant concentration beginning at intrinsic. Right: Cadmium oxide rocksalt structure with a yttrium atom (green atom) substitutionally placed on a cadmium site.

Fig. 3.5 (left) shows the electrical properties, i.e. mobility as a function of carrier concentration, for Y:CdO grown on c-plane sapphire. Initially doping with yttrium results in a slight reduction in carrier concentration from a value of $1.3 \times 10^{19}$ cm$^{-3}$ to $1.1 \times 10^{19}$ cm$^{-3}$. Similar to dysprosium, the Gibbs free energy of formation for Y$_2$O$_3$ is -1816 kJ/mol compared to CdO’s -520 kJ/mol.$^{56,55}$ Therefore, small dopant concentrations of yttrium results in an increased oxygen uptake reducing the carrier concentration while increasing the mobility (same as dysprosium doping). Note, for this effect to be seen, the rate of oxygen uptake has to be equal to or larger than the substitution of Y$^{3+}$ on Cd$^{2+}$ sites, otherwise initial yttrium doping would cause an increase in carrier concentration.
Moreover, it is possible Y’s oxidation state is 2\(^+\), providing the benefits of a low formation energy without adding electrons to the conduction band. Further investigation of Y:CdO will shed light on the mechanism responsible for the observed initial decrease in carrier concentration.

Between \(3.7 \times 10^{19}\ \text{cm}^{-3}\) and \(1.4 \times 10^{20}\ \text{cm}^{-3}\), the mobilities plateau with values in excess of 400 cm\(^2\)/Vs. Further increasing the carrier concentration past \(1.4 \times 10^{20}\ \text{cm}^{-3}\) results in a steadily decreasing mobility to a minimum value of 247 cm\(^2\)/Vs. The sharp decrease in mobility can be attributed to crystallographic defects, increased mosaicity, and compensating defects as previously discussed in the Dy:CdO system.

Y:CdO has similar, if not better, electrical properties than that of Dy:CdO. One distinct difference is the plateau in mobility observed for Y:CdO, which we believe stems from the stability of yttrium’s oxidation state. Qualitatively, yttrium’s most stable oxidation state is 3\(^+\), while dysprosium has stable 2\(^+\) and 3\(^+\) oxidation states; thus, it is plausible there exists a higher percentage of neutral dysprosium on a cadmium site compared to yttrium when doping CdO. Furthermore, a lower dopant concentration decreases the number of impurity scattering centers leading to a higher mobility. In conclusion, yttrium seems to be a superior dopant in regards to the observed electrical properties.

### 3.1.4 RF Co-sputtering Limitations

Although RF co-sputtering is an advantageous deposition technique for the growth of doped cadmium oxide, there are several disadvantages. For maximum oxygen uptake (and consequently optimal electrical properties) in doped cadmium oxide, the gas environment during RF co-sputtering was kept at 20% oxygen and 80% argon at 100 millitorr (Refer to section2.1.2). Although the growth of doped cadmium oxide favors relatively high oxygen densities and deposition pressures, these parameters present multiple experimental impediments—heavy oxidation of the sputtering targets, slow deposition rates on the order of 3-4 nanometers/minute, and unwanted anion re-sputtering. To overcome these challenges, pulsed-DC magnetron sputtering was implemented, which is the focus of the following sections. By pulsing the target on the order of microseconds, a highly reactive environment can be achieved eliminating the need for high pressure, or high oxygen densities.

The following sections continue to explore different dopants and their subsequent electronic and structural properties in the CdO system using pulsed-DC magnetron sputtering.

### 3.2 Pulsed-DC Magnetron Co-sputtering

#### 3.2.1 High Mobility Yttrium Doped Cadmium Oxide Thin Films

3.2.1.1 Abstract

Donor doped CdO thin films on c-plane sapphire are prepared by reactive co-sputtering from Cd-metal and Y-metal targets which are driven using pulsed-dc and RF power respectively. Intrinsic CdO exhibits a carrier density of \(1.8 \times 10^{19} \text{ cm}^{-3}\) and a mobility of \(330 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}\). By increasing the Y-flux, carrier density values can be increased smoothly and reproducibly to a maximum value of \(3.3 \times 10^{20} \text{ cm}^{-3}\). Mobility increases with Y flux, and exhibits a broad plateau between approximately \(5 \times 10^{19} \text{ cm}^{-3}\) and \(2 \times 10^{20} \text{ cm}^{-3}\). Higher carrier concentrations produce a sharp drop in mobility. The increase in mobility is attributed to a reduction of intrinsic donors (i.e., oxygen vacancies) with increasing carrier density while the ultimate decrease in mobility results from a combination of factors including cadmium vacancies, reduced crystal quality, and smaller crystallite sizes, all of which accompany carrier density values greater than the mid \(10^{20} \text{ cm}^{-3}\) range. This work demonstrates that CdO thin films can be prepared by magnetron sputtering with transport properties and crystal quality that are comparable to those grown using molecular beam epitaxy.

3.2.1.2 Introduction

In recent years, conductive metal oxides have been increasingly investigated in the context of electronic, plasmonics, and optical technologies. The interest in plasmonic technologies surrounds many emergent optoelectronic applications, such as plasmon lasers\(^6\)\(^5\), transistors\(^6\)\(^6\), sensors\(^6\)\(^7\), and information storage\(^6\)\(^8\). While plasmonic materials, such as gold and ITO, have been found for UV-VIS and near infrared wavelengths, the mid-infrared range remains a challenge to address due to low free carrier mobility values (i.e., high plasmonic loss) common in conductors with carrier concentrations that support plasmonic resonance in the infrared. Recently, Sachet et al. demonstrated electron mobilities surpassing \(500 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}\) at carrier densities greater than \(5.0 \times 10^{19} \text{ cm}^{-3}\) in Dy-doped CdO (CdO:Dy). These unique transport properties satisfy the criteria for mid-infrared spectrum plasmonics, and overcome the optical losses seen in conventional conductors, such as noble metals\(^5\)\(^7\). In this work, the precision doping afforded by oxide molecular beam epitaxy enables one to explore and understand the relationships between composition, defect chemistry, and electronic transport in CdO:Dy. However, the sophistication of MBE instrumentation presents a barrier for material implementation. As such, there is interest to explore if similar properties are achievable in alternative deposition methods. Furthermore, there may be additional opportunities for property optimization with techniques that can access non-equilibrium processing conditions and higher pressures and temperatures.

The thin film community explored alternative process methods to manufacture doped cadmium
oxide thin films, such as metalorganic vapor phase-epitaxy\textsuperscript{58}, pulsed laser deposition\textsuperscript{69}, colloidal nanocrystals\textsuperscript{70}, and radio frequency sputtering\textsuperscript{71}. However, there are no reports that duplicate the reported property trends of CdO:Dy in the similarly low concentration regime ($<1 \times 10^{20}$ cm$^{-3}$) needed to identify the salient defect chemistry trends. In this work we demonstrate donor doped CdO films prepared by high-power impulse magnetron sputtering (HiPIMS) where it is possible to combine the material quality of MBE with the practicality and flexibility of a magnetron sputtering infrastructure. Conventional magnetron sputtering plasmas are sustained by either DC or radio frequency (RF) power, which is typically chosen based on the target resistivity. In the past decade, deposition from pulsed DC plasmas have gained increasing attention. Using pulsed DC, one can vastly extend the power limitations typically imposed by target melting temperature or the magnetron depoling, provided the durations are short. For example, power densities on the order of 10 W/cm$^2$ are used commonly to sputter materials like HfO$_2$, In$_{1-x}$Sn$_x$O$_3$, and TiN. This produces ionization fractions on the order of 10%. In many cases, a higher ionization fraction is desired, for example, to increase oxidation in a reactive deposition, or to promote additional energetic bombardment. If ionization fractions exceed 80% a self-sputter regime can be reached where the bombarding species is primarily the target material (i.e., gasless sputtering)\textsuperscript{48}. The power densities needed to access this ionization extreme would overheat conventional cathodes if run continuously. They can, however, be sustained when operated in pulsed mode. Imposing a duty cycle where the on time is 10% and pulse duration is on the order of 100 $\mu$s achieves this condition. During these short pulses, power densities $\sim$ 1 kW/cm$^2$ can be achieved, leading to high sputter rates, advantageous substrate bombardment, high reactivity, denser as-deposited films, and a reduced surface roughness\textsuperscript{45}. The experiments presented below demonstrate that HiPIMS enables one to prepare doped CdO thin films with crystal structure, surface roughness, and transport properties comparable to MBE-grown material, and that one can co-deposit a donor dopant using an RF magnetron cathode source.

### 3.2.1.3 Experimental

Heteroepitxial thin films of CdO:Y ($\sim$150 nm) were prepared by reactive HiPIMS from a metallic Cd target (99.9999% metal basis) and by reactive RF sputtering from a metallic Y target (99.9+\% metal basis). The magnetrons are oriented slightly outside the confocal point at a horizontal substrate in sputter-down geometry with $\sim$45$^\circ$ angle of incidence. All films were sputtered in an argon-oxygen environment at 10 mTorr flowing 19 sccm Ar and 13 sccm O$_2$. The HiPIMS parameters were 800 Hz and 80 $\mu$s pulse time, this produces a 1250 $\mu$s period and 6.4% duty cycle. The HiPIMS plasma was driven by a Starfire Industries Impulse Pulsed Power Module and an Advanced Energy MDX 1.5K DC power supply, while the RF plasma was driven by an Advanced Energy RFX-600 and a Manitou Systems manual matching network. The DC power supply that feeds the HiPIMS unit was operated in constant voltage mode with a target value of 400 V. Two-inch diameter MeiVac MAK cathodes
were used for both metals.

Doping was achieved by co-sputtering. To modulate the dopant flux and ultimately the carrier concentration in the range of interest it is necessary to vary both the dopant target-to-substrate distance and the RF power. To quantify these coupled parameters, we introduce the quantity \([W/cm^4]\), which is the time averaged power density applied to the dopant cathode divided by the cathode-to-substrate distance. In the regime of carrier concentrations reported, a deposition rate of approximately 33 nm/min was maintained. Note that increasing the dopant magnetron power density had negligible effect on deposition rate.

All films were grown on epitaxial-polished c-plane sapphire substrates bonded to a stainless steel puck using silver paint. For all depositions the puck surface temperature was 370 °C and monitored by a Raytek 1.6 µm MM Series Pyrometer. All samples were annealed at 700 °C for 1 hour in flowing O\(_2\) post-deposition to optimize oxygen uptake. CdO transport properties were characterized using an Ecopia HMS-3000 Hall Measurement System. Crystal quality and lattice parameters were characterized by X-ray diffraction (XRD) using a Panalytical Empyrean XRD in parallel beam geometry employing a double bounce hybrid monochrometer for the incidence beam optic and a 0.18° parallel plate collimator. Film thickness values were determined by X-ray Reflectivity (XRR).

### 3.2.1.4 Results and Discussion

The signature experiment central to this report monitors the carrier concentration and mobility as a function of Y addition. To do so, a set of CdO films were prepared where the Y flux was increased systematically. Figure 1 summarizes the carrier concentration and mobility trends collected for this series, the most important observations include: 1) intrinsic CdO has a carrier concentration of \(1.8 \times 10^{19} \text{ cm}^{-3}\) and a mobility of \(330 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}\); 2) carrier concentration increases monotonically with increasing Y flux, up to a maximum value of \(3.3 \times 10^{20} \text{ cm}^{-3}\); and 3) mobility increases to a plateau value > 400 cm\(^2\) V\(^{-1}\) s\(^{-1}\) up to a carrier concentration of \(2.2 \times 10^{20} \text{ cm}^{-3}\), and falls rapidly as additional Yttrium is added.

CdO has a cubic rocksalt structure with a direct and indirect bandgap of approximately 2.2 eV\(^{72}\) and 0.84 eV\(^{73}\), respectively. The conductivity of undoped CdO is attributed to its intrinsic n-type behavior where sub-stoichiometric oxygen content promotes oxygen vacancy formation compensated by electrons. The high carrier concentrations at room temperature can be attributed to their shallow energy level relative to the conduction band minimum. Using hybrid DFT calculations, Burbano et al. shows that oxygen vacancies present in intrinsic CdO act as doubly ionized shallow donors, unlike all other n-type TCOs\(^{74}\).

Carrier density increases with increasing Y content and can be attributed to the following defect
chemistry reaction for dissolution of Y in a CdO lattice.

\[
Y_2O_3 \xrightarrow{\text{CdO}} 2 Y^{3+}_{\text{Cd}} + 2 O_2^- + 2 n + \frac{1}{2} O_2(g) \quad (3.2)
\]

For Y-accommodation as a 3$^+$ cation, its most stable state, every yttrium ion will be compensated by one electron. Between $2 \times 10^{19}$ cm$^{-3}$ and $2 \times 10^{20}$ cm$^{-3}$ the increase in carrier concentration is linear with power density/working distance suggesting a constant activation rate. It is interesting to note that carrier density is essentially flat for very low Y content while in the same range mobility increases sharply. Previous reports for Dy-doped CdO showed that adding aliovalent donors reduced the concentration of oxygen vacancies promoted by a Fermi level shift to larger values, which in turn increased the energetic expense of oxygen vacancy compensation and thus formation. We hypothesize that this initial plateau corresponds to the region where carriers introduced by Y are effectively balanced by a reduction of carriers that compensate oxygen vacancies, thus the flat response. In this same doping region there is a large increase in electron mobility. As for the case of CdO:Dy, this trend is explained by a reduced population of oxygen vacancy donors and replacement by Y$^{3+}$ donors. Since charged impurity scattering scales with $Z^2$, one expects less impact from 2N donors with a 1$^+$ charge with respect to the lattice i.e., Y$_{\text{Dy}}^*$ than from N donors with a 2$^+$ charge with respect to the lattice, i.e., Vo$^*$. 

From carrier densities between $2 \times 10^{19}$ cm$^{-3}$ and $2.1 \times 10^{20}$ cm$^{-3}$, mobility values are greater than 400 cm$^2$V$^{-1}$s$^{-1}$, with a small reduction towards the high end of this range. Above $2.1 \times 10^{20}$ cm$^{-3}$, the rate of free carrier generation per W/cm$^4$ reduces and there is a steep drop in mobility. In this carrier density range, one does not expect such strong carrier-carrier scattering, and it is unlikely that the curvature of the band structure changes so abruptly as to increase the effective mass. As such, alternative mechanisms must be present. It has been shown from DFT calculations that the dominating defects present in doped cadmium oxide are a strong function of the Fermi energy. For carrier densities in the $5.0 \times 10^{20}$ cm$^{-3}$ range, the Fermi level is shifted higher into the conduction band producing a strong Burstein-Moss shift. As such, the formation energy for cadmium vacancies becomes lower than that for oxygen vacancies. Thus, in this range of carrier density, additional Y donors will be compensated by a growing percentage of metal vacancies as opposed to electrons, which will contribute to charged defect scattering.

In addition, it is possible that a change in film structure accompanies this dopant range and promotes additional scattering. To test this hypothesis, we conducted atomic force microscope (AFM) and four-circle x-ray diffraction analysis to identify trends in crystallinity and surface microstructure as a function of doping level.

For epitaxial growth on c-plane sapphire the preferred crystallographic registry occurs when the (001) plane of CdO is tilted by 23.5° to sapphire (00.1) with a tilt direction parallel to sapphire <10.0>, this high-index orientation was reported by Zuniga-Perez et al., which corresponds to a (025) CdO.
plane parallel to the sapphire basal plane. Consequent to the sapphire symmetry, there are three equivalent in-plane orientations of CdO grains. Because of this tilted growth, CdO reflections are only visible to asymmetric or skew-symmetric scans. Figure 2(a) shows a series of asymmetric $\theta$-2$\theta$ scans surrounding the (220) CdO reflections as a function of yttrium doping - the (220) peak is chosen for its high relative intensity and because it can be accessed using an asymmetric configuration. There are two observations of interest: the (220) interplanar spacing of 1.656 Å agrees with the bulk value 1.661 Å; and its height and width are affected negligibly by the yttrium content, until the very highest Y concentrations; A plot of FWHM values for the (220) reflection as a function of carrier concentration (i.e. yttrium concentration) is presented in the supplemental materials section.

A companion sub-set of omega scans for the same CdO:Y doping series are presented in Figure 2(b), again for the (220) reflections. A distinct trend appears for increasing yttrium concentration. For carrier concentrations less than $6.5 \times 10^{19}$ cm$^{-3}$, the omega scans reveal a consistent FWHM value of 0.30 °. Above this range, the values broaden modestly until the very highest concentrations where mosacity increases sharply. The increase in mosacity accompanies the precipitous drop in carrier mobility.

Figure 3 displays a (111) phi scan of CdO:Y with intermediate carrier concentration of $6.1 \times 10^{19}$ cm$^{-3}$. As reported previously, CdO adopts an in-plane alignment [100] CdO $\parallel$ [01.0]. This produces
Figure 3.7 X-ray diffraction data for a subset of CdO thin films as a function of carrier concentration. (a) Theta-two theta patterns of the (220) reflection show consistently narrow peak widths while the (b) omega scans show substantial broadening with higher dopant density values.

three individual CdO orientations related by 120°, each exhibiting 1-fold rotational symmetry with respect to the substrate normal. Finally, theta-two theta scans using the Bragg-Brentano geometry and an area detector were collected for CdO thin films with the highest carrier density and may be found in the supplemental material. These optics are most sensitive to small volume fractions of material or crystallites that are highly disordered and thus poor scatterers. We find no evidence for second phase formation.

AFM images were collected for samples across the doping series to compare surface microstructure. A subset of those images are shown in the supplemental information. Most importantly, the surface images reveal a microstructure that is similar in shape and roughness across the series, but there is a dramatic (nearly 10 X) decrease in grain size that accompanies the decrease in mobility at the highest carrier density level.

While we cannot at this stage separate the extent to which each aspect regulates carrier mobility, we can conclude that a combination of increased mosaic spread of crystallites, an increased population of low angle grain boundaries, and a likely increase in compensating intrinsic defects is responsible for the mobility drop when carrier densities exceed the mid $10^{20}$ cm$^{-3}$ range. We speculate that these structural trends occur because we are approaching the solubility limit of Y in CdO, where strong crystallographic disorder precedes second phase formation.

Yttrium doped CdO thin films have been grown on c-plane sapphire via HiPIMS exhibiting char-
Figure 3.8 Phi scan of $<111>$ CdO planes showing three peaks separated by 120° indicating the presence of three equivalent in-plane orientations.
acteristics similar to that of dysprosium doping. The thin films maintain mobility values in the range of 400 cm$^2$V$^{-1}$s$^{-1}$ over the dopant range $1.8 \times 10^{19}$ cm$^{-3}$ to $3.3 \times 10^{20}$ cm$^{-3}$. X-ray diffraction analysis for all films reveals line widths in two-theta that are uniformly narrow and calculated lattice constants that are close to the bulk value. Rocking curve analysis, however, reveals substantial broadening for carrier concentrations above $2.5 \times 10^{20}$ cm$^{-3}$. A substantial drop in mobility accompanies this carrier density range. The mobility drop is likely associated with increased crystalline disorder, finer crystallite size, and a cadmium vacancy concentration that is predicted to grow in this dopant regime. MBE-grown CdO:Dy was shown to be a model semiconductor, potentially useful in a variety of applications in the mid-IR spectrum. In this manuscript we demonstrate that comparable transport properties can be achieved in sputtered CdO with Y donors.
3.2.1.5 Supplementary Material

![Graph](image)

**Figure 3.9** FWHM (degrees) of high resolution XRD omega scans as function of measured carrier concentration.

![Graph](image)

**Figure 3.10** Theta-two theta X-ray diffraction data for highest doped CdO:Y (3.3Å 10^20 cm^-3) spanning 30 to 70 degrees, aligned to the surface of the film. Data is representative of entire doping series and confirms the absence of secondary phase formation.
Figure 3.11 Atomic force microscope images of yttrium doped cadmium oxide at approximately 150 nm arranged from lowest to highest carrier concentration: a) $1.8 \times 10^{19}$ cm$^{-3}$, b) $1.3 \times 10^{20}$ cm$^{-3}$, and c) $2.3 \times 10^{20}$ cm$^{-3}$.
3.2.2 Acceptor and Donor Doping in Cadmium Oxide Thin Films

Manuscript.

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3.2.2.1 Abstract
Donor and acceptor doped CdO thin films are prepared by reactive co-sputtering from Cd-metal and dopant-metal targets which are driven using pulsed-DC and RF power respectively. The electrical and structural properties of Ag, In, Ce, and Sn doped CdO are studied. By increasing Ag-flux, electron concentrations are reduced to $5.1 \times 10^{18} \text{cm}^{-3}$ with a mobility value of $325 \text{cm}^2/\text{Vs}$. Conversely, by increasing In-flux, electron concentration values can be increased smoothly to a maximum value of $4.5 \times 10^{20} \text{cm}^{-3}$. Maximum electron concentration values are in good agreement with previous saturation electron concentration reports. Mobility values as high as $411 \text{cm}^2/\text{Vs}$ are achieved in the $10^{19} \text{cm}^{-3}$ range, following a steady drop due to increased mosaicity, compensating defects, and reduced crystal quality at higher electron concentrations. Doped cadmium oxide proves to be a model conducting metal oxide semiconductor in the $10^{18} \text{cm}^{-3}$ to $10^{20} \text{cm}^{-3}$ range.

3.2.2.2 Introduction
Engineering high mobility conducting metal oxides (CMOs) across a wide range of carrier densities is of detrimental importance for the development of electronic, plasmonic, and optical technologies. While Si and other III-V semiconductors have revolutionized modern electronics, they exhibit poor electron mobilities and optical opacity, limiting future applications. Conducting metal oxides, such as indium tin oxide (ITO), aluminum doped zinc oxide (AZO), and indium-gallium-zinc oxide (IGZO) have desirable optical properties (i.e. band gaps ranging from 2.0 to 8.0 eV), high electron mobilities, and diverse synthesis techniques (sputtering, pulsed laser deposition, evaporation etc.). However, in the carrier concentration ranges of interest for high conductivity and infrared (IR) optoelectronics, the electron mobility deteriorates by an order of magnitude, restricting the efficiency.

An interesting CMO gaining much attention for unprecedented electron mobilities is doped cadmium oxide (CdO). CdO has an impressive static dielectric constant, $\epsilon = 21.9$, in addition to low effective mass, $m^* = 0.21$, compared to that of common CMOs. Consequently, CdO maintains a high mobility at high carrier concentrations due to efficient screening of ionized impurities. Recently, Sachet et al. reported electron mobilities exceeding 500 cm$^2$/Vs with dysprosium doped cadmium oxide (Dy:CdO) epitaxially grown on magnesium oxide. In this work, molecular beam epitaxy (MBE) was utilized to establish relationships between defect chemistry, composition, and electronic properties. As such, it was found doping cadmium oxide with dysprosium results in a
Table 3.1 Carrier concentration, mobility, conductivity, thickness, synthesis method, and substrate of various doped cadmium oxide reports. MOCVD: metal organic chemical vapor deposition. SP: spark plasma. SSR: solid state reaction. Evap: evaporation. PFCAD: pulse filtered cathodic arc deposition. Asterisk denoted values extrapolated from graphed data.

<table>
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<th>Dopant</th>
<th>Carrier Concentration ([\times 10^{20}\text{cm}^{-3}])</th>
<th>Mobility ([\text{cm}^2/\text{Vs}])</th>
<th>Conductivity ([\text{S/cm}])</th>
<th>Thickness ([\text{nm}])</th>
<th>Synthesis Method</th>
<th>Substrate</th>
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<td>MgO (100)</td>
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<td>100-350</td>
<td>RF Sputter</td>
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strong Burstein-Moss shift ultimately increasing the defect formation energy for oxygen vacancies, which are the primary electron scattering centers. The reduction in oxygen vacancies as a function of dopant concentration produced high electron mobilities with carrier concentrations surpassing \(5\times10^{19}\ \text{cm}^{-3}\). With that said, the complexities associated with MBE present barriers to future materials applications. Furthermore, there still remains an interest in the optoelectronics community, amongst others, to expand carrier concentrations to the \(10^{18}\) to \(10^{21}\ \text{cm}^{-3}\).

The thin films community has exploited a number of dopants alongside synthesis techniques to engineer the electrical properties of doped cadmium oxide (Table 3.1). Although mobilities exceeding 300 \(\text{cm}^2/\text{Vs}\) have been achieved, a precipitous drop exists past the optimal carrier concentration. A key factor limiting high mobility cadmium oxide is the synthesis route. A relatively new synthesis technique known as high-power impulse magnetron sputtering (HiPIMS) offers a range of tunable parameters enabling high mobility doped cadmium oxide with a range of carrier-mobility combinations. By pulsing the cathode on the order of \(100\ \mu\text{s}\), power densities on the order of \(\text{KW/cm}^2\) can be achieved leading to ionization fractions ranging from 80% to 100%. These advantageous ionization fractions increase the propensity for oxidation, which ultimately decreases oxygen vacancies.

Herein, we present a dopant study on cadmium oxide using the aforementioned high-energy synthesis process. The following auspicious dopants were chosen based on three factors- oxidation
state, electronic configuration, and ionic radius. From an oxidation state perspective, dopants with 1+ and 4+ oxidation states are promising candidates for spanning carrier concentrations ranging from $10^{18}$ to $10^{21}$ cm$^{-3}$, illustrated by the Kroger-Vink notation:

$$\text{Cd}^\text{x}_{\text{Cd}} + \text{O}^\text{y}_{\text{O}} \rightarrow \text{Cd}^\text{x}_{\text{Cd}} + \text{V}^\text{2n}_{\text{O}} + \frac{1}{2} \text{O}_2(g) \quad (3.3)$$

$$\text{Ag} \xrightarrow{\text{CdO}} \text{Ag}^\text{Cd}_{\text{Cd}}_{\text{Cd}} + 2 \text{V}^\text{2n}_{\text{O}} + \text{h}^\text{+} \quad (3.4)$$

$$\text{MO}_2 \xrightarrow{\text{CdO}} \text{M}^\text{2n}_{\text{Cd}}_{\text{Cd}} + \text{O}^\text{y}_{\text{O}} + \frac{1}{2} \text{O}_2(g) \quad (3.5)$$

where M denotes a metal. Cadmium oxide is intrinsically a n-type CMO due to sub-stoichiometric oxygen vacancies being compensated by electrons (Eq. 3.3). Additionally, from DFT calculations, Burbano et al. shows that oxygen vacancies in cadmium oxide have a shallow energy relative to the conduction band minimum, acting as doubly ionized shallow donors, further explaining cadmium oxides intrinsic behavior. To compensate these electrons and further reduce the carrier concentration, we propose doping cadmium oxide with silver, as it is univalent (Eq. 3.4). Furthermore, silver is a viable and well-studied acceptor dopant in material systems such as zinc oxide (ZnO) and barium titanate (BaTiO$_3$). We aim to reduce the electron concentration of cadmium oxide into the $10^{18}$ cm$^{-3}$ allowing for interesting applications in the long-wave IR.

Conversely, a 4+ oxidation state would allow for higher carrier concentrations with a lower dopant concentration, relative to 3+ dopants (Eq. 3.5); thus, decreasing the level of lattice perturbation on a per electron basis, enabling a higher electron mobility. Therefore, for this higher carrier concentration realm, we propose cerium and tin as 4+ oxidation state dopants.

Lastly, indium is a prospective dopant based on its electronic configuration. An indium dopant on a cadmium site will contribute two s electrons for bonding, and the third loosely bound electron will sit in the conduction band. Also, since indiums d orbital is completely filled, there should be minimal perturbations to the conduction band. Moreover, based on its relatively close ionic radius ($\text{In}^{3+}$: 0.80 Å) to that of cadmium, minimal lattice distortion will occur minimizing additional crystallographic defects. Collectively, by choosing dopants based on oxidations state, electronic configuration, and ionic radius we propose the $10^{18}$ to $10^{21}$ cm$^{-3}$ can be accessed in the doped cadmium oxide system.
3.2.2.3 Experiment

Heteroepitaxial thin films of doped CdO (150nm) were prepared by reactive HiPIMS from a metallic Cd target (99.9999% metal basis) and by reactive RF sputtering from a metallic dopant target (Ce, Sn, Ag, and In). The magnetrons are oriented slightly outside the confocal point at a horizontal substrate in sputter-down geometry with $45^\circ$ angle of incidence. All films were sputtered in an argon-oxygen environment at 10 millitorr flowing 20 sccm Ar and 14 sccm O$_2$. The HiPIMS parameters were 800 Hz and 80 $\mu$s pulse time, this produces a 1250 $\mu$s period and 6.4% duty cycle. A Starfire Industries Impulse Pulsed Power Module and an Advanced Energy MDX 1.5K DC power supply drove the HiPIMS plasma, while an Advanced Energy RFX-600 and a Manitou Systems manual matching network drove the RF plasma. The DC power supply that feeds the HiPIMS unit was operated in constant voltage mode with a target value of 400 V. Two-inch diameter MeiVac MAK cathodes were used for both metals.

Doping was achieved by co-sputtering. To modulate the dopant flux and ultimately the carrier concentration in the range of interest it is necessary to vary both the dopant target-to-substrate distance and the RF power. In the regime of carrier concentrations reported, a deposition rate of approximately 20 to 30 nm/min was maintained. Note that increasing the dopant magnetron power density had negligible effect on deposition rate.

For all depositions the puck surface temperature was 370 °C and monitored by a Raytek 1.6 $\mu$m MM Series Pyrometer. Post deposition, all films were annealed in a static O$_2$ environment at 700°C for 30 minutes to facilitate oxygen uptake and recrystallization.

Electrical measurement, i.e. carrier concentration and mobility, were measured using an Ecopia HMS-3000 Hall Measurement system in a Van der Pauw geometry. The thin film crystal quality was measured using a Panalytical Empyrean diffractometer with an incident monochromated parallel beam and 0.18° parallel plate collimator detector. In addition, film thickness values were determined by X-ray Reflectivity (XRR).

3.2.2.4 Results and Discussion

Fig. 3.12 summarizes the electron mobility as a function of carrier concentration for the four proposed dopants (Ag,Ce,Sn, and In) in addition to previous reports of yttrium [Kelley et al.] and fluorine [Runnerstrom et al.] synthesized by similar methods. The black circles labeled intrinsic denote the intrinsic mobility-electron concentration combinations for undoped cadmium oxide. As either the acceptor (Fig. 3.12 left) or donor (Fig. 3.12 right) concentration is increased, the carrier concentration is decreased or increased, respectively. Note, the colored lines connecting the data points from 'intrinsic' indicate the direction of increasing dopant flux.

Silver doped cadmium oxide (Ag:CdO) electrical data is shown in Figure 1 (blue diamonds). Ag:CdO thin films were grown on MgO(100) to minimize lattice mismatch in efforts to decrease the
number of intrinsic defects, i.e. oxygen vacancies. Therefore, cadmium oxide epitaxially grown on MgO(100) has fairly high intrinsic mobility of 444 cm$^2$/Vs. As the silver concentration is increased, a steadily decreasing carrier concentration is observed reaching a minimum of $5.1 \times 10^{18}$ cm$^{-3}$ with a mobility of 325 cm$^2$/Vs. The decreasing carrier concentration can be attributed to the electronic compensation of Ag$^{1+}$ (Eq. 3.4). Increasing the silver flux past the minimum resulted in a stark increase in carrier concentration. When six coordinated, silver has an ionic radius of 1.15 Å, which is 19% different. Therefore, at elevated dopant concentrations, one would expect significant lattice distortions, inducing various charge scattering defects. This effect is seen by significant broadening in omega XRD scans, indicating an increase in mosaicity, alongside a precipitous drop in mobility. A comprehensive XRD study of Ag:CdO on MgO can be found in the Supplementary Information section.

Cerium (Ce:CdO) and tin (Sn:CdO) doped cadmium oxide were grown on c-plane sapphire shown in Fig. 3.12. Upon initially doping, the two dopants display a significant discrepancy between maximum mobility values. Cerium exhibits a maximum mobility value of 323 cm$^2$/Vs, while tin is substantially lower at a value of 258 cm$^2$/Vs. Cerium has an ionic radius of 1.01 Å, or 5% different
Figure 3.13 High resolution X-ray diffraction. Left) Two-theta Omega scans and Right) Omega scans of tin, indium, and cerium doped cadmium oxide at similar carrier concentrations.

than cadmium, and tin has an ionic radius of 0.69 Å, or -32% different than cadmium. Qualitatively, the large difference in mobilities can be attributed to the scattering mechanisms associated with large dopant misfits. Both dopants exhibit a monotonically increasing carrier concentration with dopant flux, reaching maximum carrier concentrations of $1.7 \times 10^{20}$ cm$^{-3}$ (Ce:CdO) and $4.1 \times 10^{20}$ cm$^{-3}$ (Sn:CdO). Note, the mobilities at these concentrations were 255 cm$^2$/Vs and 190 cm$^2$/Vs, respectively. It is possible cerium's relatively low maximum electron concentration, compared to that of tin, can be attributed to a 3+ oxidation state, rather than a 4+ oxidation state. This is suggested from the factor of 2 difference in maximum electron concentrations. In any case, both dopants demonstrate donor doping CdO with mobilities in excess of 200 cm$^2$/Vs.

Indium was the most promising dopant with a maximum mobility of 411 cm$^2$/Vs at an electron concentration of $5.2 \times 10^{19}$ cm$^{-3}$ on c-plane sapphire. Between $5.2 \times 10^{19}$ cm$^{-3}$ and $2.0 \times 10^{20}$ cm$^{-3}$ a parabolic maximum in mobility is observed. As discussed in the introduction [Sachet], the sharp rise in mobility is associated with the Burstein-Moss shift increasing the formation energy of oxygen vacancies, reducing the density of scattering centers. The maximum carrier concentration for In:CdO is $4.5 \times 10^{20}$ cm$^{-3}$ with a mobility of 213 cm$^2$/Vs, which surpasses the previously mentioned Ce, Sn, F, and Y dopants. From an ionic radius and electronic compensation perspective, indium is similar to that of yttrium and fluorine, yet the maximum carrier concentration is over 30% higher. This suggest indium has a favorable bonding scheme due to the similar electronic configuration to that of cadmium.

For In, Sn, and Ce in Fig. 3.12, the carrier concentration begins to decrease when past the maximum mimicking a hook-like shape. This behavior suggest a compensating mechanism, most
likely cadmium vacancies, is reducing the carrier concentration. It is interesting to note Ce has a substantially lower "carrier concentration hook". Presumably, the formation energy of a cadmium vacancy is lower than creating more crystallographic defects associated with a dopant on a Cd site.

For Sn and In, the maximum carrier concentration achieved is in the $4 \times 10^{20}$ cm$^{-3}$ range. In addition to the previously proposed mechanism for creating cadmium vacancies, there also exists a Fermi stabilization energy. The effects of a Fermi stabilization energy limiting carrier concentrations can be seen in all semiconductor systems from InN$^{90}$ to Ge$^{91}$ and GaN$^{92}$. The maximum carrier concentration measured for In and Sn is consistent with reports of the Fermi stabilization energy lying approximately 1 eV above the conduction band minimum. L.F. Piper et al. have shown through angle-resolved photo-emission spectroscopy that the Fermi level at the CdO free surface is pinned at $\sim 1.15$ eV$^{81}$. Similarly, D.T. Speaks et al. report the Fermi level lying $\sim 1$ eV above the conduction band minimum, resulting in a saturation of the electron concentration of $4.5-5.0 \times 10^{20}$ cm$^{-3}$.$^{93}$ Following the amphoteric-defect model, shifting the Fermi level higher than the Fermi stabilization level will only result in compensating defects, i.e. cadmium vacancies. Therefore, we strongly believe the maximum concentration obtained using In and Sn can be attributed to the large Burstein-Moss shift as a function of dopant concentration approaching the Fermi stabilization energy, giving rise to compensating defects. Note, for a number of dopants used in Table 1, the maximum electron concentrations exceed the saturation limit; thus, the possibility of additional carrier mechanisms increasing the electron concentration cannot be ruled out.

For epitaxial growth on c-plane sapphire, the preferred crystallographic registry occurs when the (100) plane of CdO is tilted by 23.5° relative to sapphire (0001), as previously reported [K.P. Kelley et al.]. Since CdO reflections are only visible in asymmetric or skew-symmetric scans, Fig. 3.13 (left) shows a series of X-ray diffraction (220) CdO peaks for all three donor dopants in the intermediate electron concentration range close to the mobility maximum. The lattice constant is consistent for all three dopants ($\sim 1.656$ Å), indicating negligible lattice perturbations as a function of dopant. A companion set of omega scans are presented in Fig. 3.13 revealing consistent FWHM values of $\sim 0.30°$, concluding both mosaicity and lattice parameter are equivalent near the peak mobility for all three dopants.

### 3.2.2.5 Conclusion

We have presented an experimental study of high mobility doped cadmium oxide using a variety of dopants. All dopants successfully shifted the electron concentration to higher and lower values, while maintaining relatively high mobilities. The minimum and maximum electron concentrations obtained were $5.1 \times 10^{18}$ cm$^{-3}$ and $4.5 \times 10^{20}$ cm$^{-3}$ for silver and indium, respectively. We believe the minimum electron concentration achieved in silver doping occurs due to an increased mosaic spread of crystallites, confirmed from XRD, resulting in an increased population of low angle grain
boundaries ultimately increasing the density of defects, or oxygen vacancies. Moreover, the maximum electron concentration limitation is twofold—crystallographic defects and approaching the Fermi stabilization energy both result in compensating defects. The effect of compensating defects can be seen by the hook shape in Figure 1. This manuscript offers insight into feasible dopants and synthesis techniques to achieve high mobility in CdO, and possible other oxide systems.

3.2.2.6 Supplementary Information

![Graph showing high resolution X-ray diffraction](image)

**Figure 3.14** High resolution X-ray diffraction. Left) Two-theta Omega scans and Right) Omega scans of silver doped cadmium oxide with increasing carrier concentration in the upward direction.
4.0.1 Abstract

Indium doped cadmium oxide homostructures are monolithically grown demonstrating superimposed Epsilon-Near-Zero (ENZ) properties. Implementing the advantageous thin film synthesis method, i.e. high-power impulse magnetron sputtering, the homostructures were grown with a high degree of crystallinity, donor segregation, and excellent electrical properties confirmed with X-ray diffraction, secondary ion mass spectroscopy, and Hall measurements. By increasing the In-flux, the plasma frequency of the multilayer system was tuned from approximately 2800 cm$^{-1}$ to 4600 cm$^{-1}$ with absorption ranging from 90% to 97%, coincident with full width half maximum values as narrow as 307 cm$^{-1}$. Additionally, by introducing thermal energy into the multilayer system,
tailored multispectral emission was observed. This work demonstrates that In: CdO homostructures are capable of unprecedented ENZ properties enabling future plasmonic applications.

4.0.2 Introduction

Engineering light-matter interactions in the infrared spectrum is of keen interest to the materials science, photonics, physics, and biophysics communities. That interest arises from opportunities for advanced communication platforms, chemical sensing, optical characterization, energy harvesting, and catalysis. A central feature threading through this diverse application space is a core ability to concentrate light’s electric field into a localized physical geometry. Noble metals patterned or formed into nanoscaled shapes are perhaps the most common embodiment enabling this. In such cases, it is possible to couple light into localized surface plasmon polaritons directly from free space. Since the metal carrier concentration is fixed, one must use geometry to engineer the polaritonic response. While it is possible to access wide frequency spectrum, elemental metals can be lossy (due to low carrier mobility) which limits the quality factor of the excitation. Furthermore, such metallic structures typically feature dimensions on the order of several tens of nanometers, which presents practical challenges of patterning, particularly over larger areas. This combination of loss and processing expense introduce barriers to application and integration.

An alternative approach to photon compression can be appreciated in an epsilon near zero mode (ENZ). This mode offers extreme sub-wavelength confinement of electric fields and can be realized in a thin slab of conductor bounded by a dielectric medium. In such a geometry, evanescent fields associated by each metal-dielectric interface couple and split into a high energy symmetric mode and a lower energy asymmetric mode. The high energy mode approaches the bulk plasmon energy and is fully expressed when the conductor layer is on the order of $\frac{\lambda}{50}$. The ENZ name originates from the fact that the mode energy exists at the bulk plasma frequency, this is by definition the frequency where the real part of the permittivity is zero. This offers a lithography-free avenue to create structures that support these interesting modes, but unfortunately, the high carrier density of elemental metals requires that such layers be impractically thin, i.e., 2 nm, and the mode energies would be well outside of the IR spectrum. A recent review by Campione et al. quantifies this mode evolution and categorizes different material families in terms of their suitability.

The IR nanophotonics community addressed this issue by employing conducting metal oxide thin films in thin layer plasmonic architectures to realize this ENZ condition. Luk et al. demonstrated ENZ coupling in the near IR to thin ITO, while Runnerstrom et al. demonstrated mid-IR ENZ coupling in F-doped CdO. The lower carrier densities and smaller permittivity values enable one to access IR frequency oscillations, whose larger skin depth leads to layer thickness values that are experimentally tractable. Furthermore, the large skin depth affords the ability to access multiple ENZ modes buried in a single structure.
In this manuscript, we build upon these concepts to explore new functionalities that might arise from multilayer homoepitaxial stacks of In:CdO where individual layers are doped to support ENZ modes through the mid-IR spectral range. The strong Bureinstien-Moss shift that accompanies these changes in carrier density, and the ability to prepare epitaxial multilayers where abrupt changes in carrier density can be "grown-in" suggests that we can make a novel type of metamaterial that has virtually no physical interfaces. Metamaterial contrast arises from permittivity changes in the range where epsilon approaches zero, and one can transition from conductor to dielectric (at a specific frequency of interest) by small changes in donor density. This exploration is performed experimentally in sputtered CdO thin film doped with In donors. Plasmonic modes are probed using IR reflectivity and emission spectra and compared to calculated optical responses based on Maxwell’s equations and a finite element solver.

4.0.3 Experimental Procedure

CdO thin films were prepared by pulsed DC magnetron reactive co-sputtering from a Cd (99.9999% metal basis) metal target and an In (99.99% metal basis) metal target. The magnetrons are oriented slightly outside the confocal point at a horizontal substrate in sputter-down geometry with an approximate 45° angle of incidence. All films were sputtered in an argon-oxygen environment at 10 mTorr flowing 20 sccm Ar and 14 sccm O₂. The pulsed DC parameters were 800 Hz and 80µs pulse time, producing a 1250 µs period and 6.4% duty cycle. A Starfire Industries Impulse Pulsed Power Module and an Advanced Energy MDX 1.5K DC power supply drove the pulsed DC plasma, while an Advanced Energy RFX-600 and a Manitou Systems manual matching network drove the RF plasma. The DC power supply that feeds the pulsed DC unit was operated in constant voltage mode with a target value of 400 V. Two-inch diameter MeiVac MAK cathodes were used for both metals.

Doping was achieved by co-sputtering. To modulate the dopant flux and ultimately the carrier concentration in the range of interest it is necessary to vary both the dopant target-to-substrate distance and the RF power. In the regime of carrier concentrations reported, a deposition rate of approximately 23 nm/min was maintained. Note that increasing the dopant magnetron power density had negligible effect on deposition rate.

All films were grown on double sided epitaxial-polished r-plane sapphire substrates bonded to a stainless steel puck using silver paint. For all depositions the puck surface temperature was 370°C and monitored by a Raytek 1.6 µm MM Series Pyrometer. All samples were annealed at 700°C for 30 minutes in a static O₂ environment to optimize oxygen uptake.

In:CdO transport properties were measured using an Ecopia HMS-3000 Hall measurement system with a 0.51 T magnet implementing a square Van der Pauw method. Thickness were measured by X-ray Reflectivity (XRR) using a Panalytical Empyrean XRD with a incident double bounce hybrid monocrimated beam optic and parallel plate collimator (0.18°). Crystal quality was characterized
using a Bragg-Brentano HD divergent optic with a 1D scanning line Pixel 3D detector (Panalytical Empyrean XRD).

ToF-SIMS analyses were performed using an ION-TOF TOF-SIMS V instrument with cesium source for sputtering and bismuth liquid metal ion gun (LMIG) source in interlaced sputtering mode for analysis. For the depth profiles, a Cs+ beam with 1 keV energy and 8 nA current was rastered over a 120 x 120 µm area. The Bi3+ beam was 0.4 pA at 25 keV and rastered over a 50 x 50 µm area at the center of the sputtered crater. The angle of incidence was 45° from normal for both beams.

Reflectivity data was obtained using a Woollam IR-VASE ellipsometer with a custom-built aluminum sample stage to allow for the Kretschmann-Raether configuration. A 90° calcium fluoride (CaF2) prism was used to couple IR light into the plasmonically active samples. To ensure good optical contact between the substrate and prism, 1.720 index-matching fluid was used (Cargille Series M). All reflectivity data was recorded with p- and s-polarized light and plotted as \( R = r_p / r_s \).

Simulated reflectivity maps were generated from a multilayer transfer-matrix algorithm employing a modified Nelder-Mead simplex optimization. In obtaining the modeled dielectric function essential to calculate the optical properties, a lossy Drude electron plasma model was employed using an effective mass of 0.21 and a high frequency dielectric constant of 5.5. Included in the transfer-matric algorithm is the dispersion relationship for a 90° calcium fluoride prism and sapphire substrate in the Kretschmann-Raether configuration to match the experimental setup. The electric field profiles were simulated using the Finite-Difference Time-Domain (FDTD) software Lumarical.

Emission measurements were taken using a Bruker Vertex 80v Fourier transform infrared (FTIR) spectrometer in combination with an external 3 axis rotational micrometer heating stage. The emission spectra were processed by dividing the emission at a given angle by the emission at surface normal, where there is no emission contribution from the ENZ heterostructure.

### 4.0.4 Results and Discussion

To demonstrate proof of concept, we design stacks of three In:CdO ENZ layers where each is tuned for the perfect absorption condition (i.e., thickness and carrier density that satisfy Equation 2 for 100% ENZ absorption). The carrier density values required were first calculated assuming that CdO can be modeled using a complex dielectric function implementing a lossy Drude electron gas:

\[
\epsilon(\omega) = \epsilon_1 + i \epsilon_2 = \epsilon_\infty - \frac{\omega_p^2}{\omega(\omega + i \gamma)}
\]

where \( \epsilon_1 \) and \( \epsilon_2 \) are the real and imaginary parts of the complex dielectric function, \( \epsilon_\infty \) is the high frequency dielectric function, \( \omega \) is the angular frequency, \( \gamma \) is the dampening term, which
Figure 4.1 Electrical and structural properties of three-layer indium doped cadmium oxide. a) Time of flight secondary ion mass spectroscopy measuring indium (black), aluminum (green), and cadmium (red) content. Silvaco electronic simulations (blue) of electron concentration within the homosturcure. b) X-ray diffraction two-theta-omega scans of homosturcture on r-plane sapphire.

is inversely proportional to the electron mobility, and \( \omega_p = \sqrt{\frac{n e^2}{m_e \varepsilon_0}} \) is the plasma frequency. The effective electron mass \( m^*_e \) for intrinsic cadmium oxide is 0.21. Justification for this was reported by Sachet et al. \(^{57} \). To sustain a perfectly absorbing ENZ plasmonic mode, the following criteria must be satisfied where a conductor is sandwiched between dielectric layers, \([100] \):

\[
1 + \frac{\varepsilon_1 k_{z3}}{\varepsilon_3 k_{z1}} = i \frac{k_{z2} d}{ \varepsilon_3 k_{z2}^2 + \varepsilon_1 k_{z2}^2 } \tag{4.2}
\]

Here, \( k_{z2}^2 = \varepsilon_1 k_{z2}^2 - k_x^2 \) is the longitudinal wave number with \( \text{Re}(k_z) + \text{Im}(k_z) \geq 0 \) in medium \( i = 1, 2, 3 \) (1 = sapphire substrate, 2 = CdO, 3 = air), \( k_x \) is the transverse wave number, \( \varepsilon_i \) is the layer relative permittivity, and \( d \) is the thickness of the conductor. The required conductor thickness for total absorption is on the order of 10’s of nanometers; thus, adjacent conductor layers in a three ENZ layer homostructure can be ignored when determining thickness and carrier density needed to satisfy Eq. 4.2.

For the three ENZ system to span the mid-IR, we engineered the electrical properties and thickness satisfying Equation 2 such that the ENZ absorption frequencies, \( \omega_{ENZ} \), range from approximately 2800 cm\(^{-1}\) to 4600 cm\(^{-1}\). Knowing that the dopant concentration, and ultimately carrier density, will affect the ENZ frequency of each layer, we investigated the degree of dopant segregation between layers of the homostructure via time of flight-secondary ion mass spectroscopy (ToF-SIMS). ToF-SIMS data provides clear evidence of dopant segregation between layers seen in
Figure 1a (black data). In this range of dopant concentrations, i.e. well below 1%, one can assume indium acts as a singly ionized dopant providing a single charge carrier. To understand the degree of electronic segregation, or in other words depletion widths, Silvaco simulations were performed using a band-to-band standard and Fowler-Nordheim tunneling models, assuming a uniform distribution of indium in each layer (Figure 1a, blue data). Material properties for the Silvaco simulations can be found in the Supplementary Section. The ratio of carrier concentration from layer to layer follows a similar trend as the dopant concentration, i.e. they both increase by a factor of two. Most importantly, the depletion width between layers was less than 2 nm seen in the band alignment from Silvaco calculations. The relatively small depletion widths and segregated layers afford the ability to grow these homostructures while maintaining discretized carrier concentrations or ENZ plasma frequencies.

In addition to the dopant distribution, the crystal quality plays a significant role in the development of metameterials. It is well known that imperfections, such as point defects, additional orientations, and dislocations can impede the sustainability of various plasmon polariton modes due to degrading electrical properties. Therefore, the structural properties were characterized using high resolution X-ray diffraction. Figure 1b depicts the XRD pattern for the three ENZ homostructure. For epitaxial growth on r-plane sapphire, the preferred crystallographic growth direction of In:CdO was (200). The presence of layering did not lead to observable changes in the orientation of the crystal structure, suggesting that the bulk metamaterial is virtually a monolithic structure. Supporting structural data is presented in the Supplementary Section.

To probe the plasmonic response, we simulated and measured the reflectivity spectra as a function of incident angle and energy. For all measurements, the ENZ mode was accessed using the Kretschmann-Raether configuration, where light is prism-coupled into the conductor, illustrated in Figure 2d. Additionally, the ENZ mode is a transverse-magnetic (TM) mode, thus only p-polarized light will couple to the plasmon plariton. Therefore, these data are distilled into intensity maps of $R_p/R_s$ (p-polarized and s-polarized reflected light) as that allows one to visualize the plasmon polariton dispersion.

Figure 2 (a)-(c) shows $R_p/R_s$ reflectivity maps of wavenumber versus incident angle for single layer ENZ thin films. To achieve maximum absorption of p-polarized light, the thickness of the films was decreased from 90 nm to 40 nm as the carrier concentration increased, satisfying Equation 2. The resulting ENZ thin films have 90% to 97% absorption, coincident with sharp full width half maximum (FWHM) values as narrow as 307 cm$^{-1}$ and quality factors as high as 14.9 (ratio of peak energy to peak width). It can be seen that the energy dispersion of the individual ENZ layers remain quite constant, a well-known characteristic of ENZ dispersion. Increasing the electron concentration of the CdO thin films, effectively blue-shifting the epsilon crossing zero point, modified the plasmonic properties of the ENZ films such that $\omega_{ENZ}$ increased from approximately 2793 cm$^{-1}$ to 4637 cm$^{-1}$ (at a 45° incidence angle). Note that the sharp absorption features, i.e. FWHM, can be attributed
Figure 4.2 Reflectivity measurements, geometry, and simulations of ENZ modes. a-c) Measured reflectivity maps of single layer ENZ thin films. d) Standard Kretschmann configuration for measuring ENZ modes. e) Transfer matrix method reflectivity simulation and f) measured reflectivity of three-layer In: CdO homostructure. All reflectivity maps are plotted as p-polarized/s-polarized reflected intensity.
to a low dampening coefficient that is proportional to the electron mobility. A comprehensive study evaluating the electrical properties of indium doped cadmium oxide can be found in the Supplementary Section. The single layer thin films provide a confirmation of ENZ modes in In:CdO, and an ENZ energy reference for the homostructure ENZ modes.

Figure 2 (e)-(f) shows a simulated and measured dispersion map of the three-layered system composed of the aforementioned single ENZ layers. The transfer matrix simulation accurately captures the unique features in the measured dispersion map, providing a powerful tool for modeling plasmon polariton modes in an experimental setup. Note, the key dissimilarity between the measured single layers and homostructure is the ENZ absorption present at 2800 cm⁻¹. As absorption is achieved at higher angles or $k_x$ values ($k_x = \omega / c \sqrt{\varepsilon_i} \sin(\theta_i)$ where $\theta_i$ is the incident angle relative to the multilayer interface) for the lower energy layer, the relatively flat dispersion curve is red shifted and significantly attenuated. The red shift at higher angles, or $k_x$ values, can be attributed to the development of a surface plasmon polariton (SPP) mode comprised of all three layers. Details regarding the transition from an ENZ mode to a SPP mode has been reserved for a later publication. S. Campione et. al. shows this transition theoretically by changing the thin film layer thickness over an appreciable range with respect to the materials skin depth. With the exception of the lower energy branch being modified by the overall development of a SPP, the individual ENZ layer resonant energy match the homostructures resonate energies quite well. From a bulk metamaterial perspective, we have successfully demonstrated the ability to bury multiple ENZ modes or resonators within in a monolithic structure.

To complement mid-IR absorption, we investigate thermal emission of the three ENZ homostructure. Kirchhoff’s law of thermal radiation states the emissivity of a material body is equal to the absorptivity at thermal equilibrium given a specific wavelength and polar angle. Thus, one would expect the three ENZ structure thermally emits radiation at $\omega_{ENZ}$ with an angular dependence. To confirm thermal emission, similar ENZ structures were fabricated, where the different In:CdO layers (similar ENZ frequencies as previous) were grown on a platinum IR mirror to facilitate forward direction emission. The emission spectra for the ENZ thin films at 400°C are plotted in Figure 3. There are several characteristics of interest: i) the single layers and multilayer emitters have similar emission wavelengths, confirming the same relationship seen in the absorption spectra. ii) The ENZ thermal emission has a polar angle dependence centered around 65°. Considering the Brewster angle (i.e. the angle of incidence where all p-polarized light is transmitted through an interface) for CdO is approximately 65°, one would expect the highest intensity of thermal emission to occur here. iii) The FDTD simulations of thermal emission and angular dependence capture the superposition of emission wavelengths and the effects of CdO’s Brewster angle. Although several groups have shown the thermal emission of an ENZ mode, it is unprecedented for a monolithic structure with multiple tailored wavelengths to have the same effect.
Figure 4.3 Simulated and measured emission angle dependence at 400°C. Top left- measured emission from individual ENZ thin films. Bottom left- measured and finite element solver simulation of multilayer ENZ homostructure emission. Top right- measured angle dependence of multilayer emission. Bottom right- finite element solver simulation of emissions angle dependence. Colors blue, green, red signify high energy, middle energy, and low energy ENZ layers, respectively.
4.0.5 Conclusion

We have successfully demonstrated that an indium doped cadmium oxide homostructure with multiple ENZ modes in a monolithic structure possesses the distinct characteristics of single ENZ thin films. The ability to synthesize multilayer doped cadmium structures with fine control over dopant segregation enables the realization of these structures which bear 3D meta-properties. Further, we confirm this relatively unique homostructure emits radiation at $\omega_{ENZ}$ following Kirchoff’s law of radiation. In conclusion, In: CdO homostructures have great potential in photonics, plasmonics, and physics due to their ease of tunablility alongside accessible synthesis routes.
Chapter 5

Hybrid Modes: Rabi Splitting

5.1 Polaritonic Hybrid-Epsilon-Near-Zero Modes: Engineering Strong Optoelectronic Coupling and Dispersion in Doped Cadmium Oxide Bilayers

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5.1.1 Abstract

Plasmonic materials and metamaterials that sustain epsilon-near-zero (ENZ) modes offer the opportunity to design light-matter interactions at the nanoscale through exotic behaviors like resonant perfect absorption and extreme sub-wavelength light concentration. Unfortunately, the utility of ENZ modes thus far has been limited because they are dispersion-less; in other words, ENZ modes have extremely low group velocities and propagation lengths, which limits their ability to transfer information without loss. We overcome this limitation here by coupling ENZ modes to surface plasmon polariton (SPP) modes in doped cadmium oxide ENZ-on-SPP bilayers. What
results is a strongly coupled hybrid mode, characterized by large Rabi splitting energies on the order of 1/3 of the mode frequency, that exhibits the desirable characteristics of both ENZ and SPP modes through simultaneous strong field confinement and propagation. Furthermore, these so-named polaritonic hybrid-epsilon-near-zero (PH-ENZ) modes are highly tunable with changes to the ENZ layer thickness and the spectral overlap of the ENZ/SPP bilayers.

5.1.2 Main Text

Extraordinary light-matter interactions become possible when the effective dielectric permittivity of a material vanishes. These so-called epsilon-near-zero (ENZ) phenomena occur near the frequency at which the dielectric function changes sign and are characterized by electromagnetic modes with light wavelengths diverging toward infinity along with decoupled spatial and temporal electromagnetic fields.\(^\text{108}\) Harnessing this behavior has recently become a major objective in nanophotonics research; examples include resonant perfect light absorption in deeply sub-wavelength thin films,\(^\text{101,109,100,102}\) wave-front engineering,\(^\text{96}\) controlled thermal emissivity,\(^\text{110}\) and extraordinary transmission by photonic tunneling.\(^\text{94}\) Practically, an ENZ condition can be realized in any material or system where the real part of the effective dielectric function passes through zero, and thus occurs naturally in materials such as doped semiconductors\(^\text{109,102,111}\) and polar crystals.\(^\text{112,113}\) Plasmonic "ENZ modes" in these materials strongly confine light and electric fields within deeply sub-wavelength films and can be used for applications like resonant perfect absorption. ENZ modes, however, have a distinct disadvantage: they are dispersion-less (i.e., their resonant energy does not change with incident wavevector), which implies that ENZ modes have a (near-)zero group velocity and thus cannot be used when energy propagation is desired. ENZ behavior (with propagation) can also be engineered within artificially-structured metamaterials\(^\text{114}\) which, to this point, have used combinations of metallic and dielectric components to produce an effective medium with a dielectric function crossing zero at the desired frequency. Due to the metallic inclusions, however, this approach has the significant drawback of high losses resulting from a high imaginary component. Most ENZ metamaterials additionally require complicated and laborious fabrication processes including electron beam lithography or direct writing by focused-ion beam milling.\(^\text{114}\) As such, there is a clear motivation to overcome these issues of loss and non-dispersion by combining low-loss natural ENZ materials within layered or otherwise engineered structures. Doing so offers the potential for new control over the modal dispersion, group velocity, propagation lengths, and operating frequencies in nanophotonic devices based on ENZ modes.

Doped semiconductors can naturally sustain ENZ behavior near the screened plasma frequency.\(^\text{102,111}\) By virtue of carrier concentrations that are tunable via doping, semiconductors exhibit spectrally tunable ENZ behavior, especially in the infrared (IR).\(^\text{115}\) However, most materials, when sufficiently doped to resonate at the energies of interest in the near- to mid-IR, suffer a corre-
sponding drop in carrier mobility due to ionized impurity scattering, which prohibitively increases optical losses in a manner similar to free carrier scattering or interband transitions in metals. This effectively limits the useful spectral range and tunability of most doped semiconductors, since the plasma frequency is proportional to the square root of carrier concentration. Polar semiconductors and dielectrics provide an important exception, as they can support ENZ modes through optically-active phonons, where the real part of the dielectric function crosses zero near the longitudinal optical (LO) phonon frequency. Such materials exhibit drastically reduced optical losses that are inherent to phonon scattering, but because the ENZ condition is material-dependent, tunability is limited. An ideal natural ENZ material would therefore exhibit wide spectral tunability in the IR (tunable carrier concentration) combined with low optical losses (high mobility). Doped cadmium oxide (CdO) satisfies these criteria, as thin films have recently been shown to support tunable carrier concentrations ranging from $10^{19}$ to $10^{21}$ e-/cm$^3$, with carrier mobility in excess of 300 cm$^2$/Vs over nearly the entire composition range (peak: 500 cm$^2$/Vs). Thus far, CdO appears to be unique amongst oxide and covalent semiconductors in its ability to combine high mobility with such broadly tunable carrier concentrations. Optically, CdO experimentally supports tunable, low-loss surface plasmon polaritons (SPPs) and ENZ modes over the entire mid-IR ($\sim$2.5-9 µm) with quality factors up to 9. This makes CdO an ideal material system to demonstrate and develop SPP and ENZ physical phenomena in the mid-IR. However, there are limitations to the practical application of singular SPP or ENZ modes—namely, although the advantages of ENZ modes include strong field confinement within the film interior and nominal insensitivity to surface imperfections, ENZ modes occur at a single frequency with flat spectral dispersion, which results in ultra-slow optical mode propagation due to the near-zero group velocity. This limits the implementation of ENZ films in applications such as waveguide design, where some of the extraordinary behaviors would be most beneficial. Conversely, plasmonic (i.e., SPP) modes propagate at much faster group velocities, but the strong interfacial confinement renders them highly sensitive to surface morphology and carrier scattering losses. One potential strategy for simultaneously overcoming the shortcomings of SPP and ENZ modes is to create a coupled hybrid mode in a single bilayer system.

Coupling of photonic and/or electronic states occurs when the two states can interact strongly. For instance, strong coupling enables Bose-Einstein condensates and cavity-coupled vibrational polaritons. A coupling interaction at a degenerate energy state changes the spatial dispersion of the two modes, which repel to result in symmetric and antisymmetric modes with a well-defined split in energy (Rabi splitting). Notably, this changes the properties of both modes and introduces new physics associated with the hybrid mode. The most well-known examples result from coupling between a high quality optical resonators and excitons in dye molecules, J-aggregates, and quantum dots. Similar effects have also been observed between two photonic states in split ring resonators coupled to plasmonic modes. Here, we demonstrate strong-coupling between SPP and ENZ modes in tunable homoepitaxial CdO ENZ-on-
SPP bilayers. The coupling is characterized by a very large and tunable Rabi splitting that is on the order of the mode frequency itself. The result is a hybrid of both SPP and ENZ modes—with high field confinement characteristic of the ENZ and fast mode propagation characteristic of the SPP—which we call a polaritonic hybrid-epsilon-near-zero or "PH-ENZ" mode. We demonstrate that coupling in PH-ENZ modes is highly tunable by varying either the carrier concentration or thickness of the ENZ layer. This paves the way for combining the benefits of ENZ and SPP behaviors in "natural metamaterials."

Each of the bilayer structures in this study contains a 300 nm-thick indium-doped CdO (In:CdO) heteroepitaxial layer grown on r-plane sapphire using reactive high-power impulse magnetron sputtering (R-HiPIMS). This 300 nm-thick In:CdO layer (hereafter referred to as the "SPP layer") has an electron concentration of $2.5 \times 10^{20} \text{e}^{-}/\text{cm}^3$, a mobility of 375 cm$^2$/Vs, and exhibits strong angle-dependent absorption due to polaritonic dispersion across the mid-IR when probed in the Kretschmann configuration; this is characteristic of a SPP mode (Fig. 5.1a). To create bilayers, a second, homoepitaxial In:CdO layer (the "ENZ layer") with controlled thickness and electron concentration is grown on top of the SPP layer. (See Fig. 5.6 for structural characterization of a representative bilayer sample.) We note that sample fabrication requires no lithography, patterning, or other micro-/nanofabrication. The corresponding dispersion relation of a representative single 100 nm-thick ENZ layer doped to $8.1 \times 10^{19} \text{e}^{-}/\text{cm}^3$ (400 cm$^2$/Vs), also measured in the Kretschmann configuration, is presented in Fig. 5.1b. The strong, dispersion-less absorption feature observed here is characteristic of an ENZ mode.

However, the dispersion relationship is drastically modified within the bilayer system. As observed in Fig. 5.1c, the bilayer sample exhibits a clear anti-crossing between the ENZ and SPP modes, which results in the dispersion splitting into upper and lower branches that acquire dispersive character over a significant part of the measured spectral range. The anti-crossing occurs where the ‘bare’ ENZ and SPP modes cross, which opens up a transparency window. This is a clear signature of strong coupling between the two electromagnetic modes at this energy, resulting in a Rabi splitting of about 717 cm$^{-1}$. To confirm this interpretation, we modeled strong coupling between an ENZ and SPP mode using the following expression:$^{127,129}$

$$E^{UB, LB\text{ coupled}}_{kx} = \frac{E_{SPP}(kx) + E_{ENZ}(kx)}{2} \pm \frac{1}{2} \sqrt{\left[E_{SPP}(kx) - E_{ENZ}(kx)\right]^2 + \left(\omega^2_R + (E_{SPP}(kx) - E_{ENZ}(kx))^2\right)^{1/2}}$$ (5.1)

Where $E^{UB, LB\text{ coupled}}_{kx}$ is the dispersion relation of the coupled upper and lower branches (UB/LB), $E_{SPP}(kx)$ is the dispersion relation of the uncoupled SPP mode, and $E_{ENZ}(kx)$ is the dispersion relation of the ENZ mode.

$k_x = \frac{\omega}{c} \sqrt{\frac{\varepsilon_1(\varepsilon_1 + \varepsilon_2)}{\varepsilon_1}}^{1/2}$ where $\varepsilon_1$ is the effective dielectric constant of the dielectric medium (here, set to 2 to roughly account for the combined presence of the ENZ layer and air above the SPP layer), and $\varepsilon_2(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + \gamma^2}$ is the dielectric function of the plasmonic layer ($\varepsilon_\infty$, $\omega_p$, $\gamma$: high frequency dielectric constant, plasma frequency, dampening frequency).
Figure 5.1 a) IR reflectivity spectral map of a bare SPP mode in the Kretschmann configuration. The In:CuO film is 300 nm thick and has an electron concentration of $2.5 \times 10^{20}$ e-/cm$^3$. b) Reflectivity map of a bare ENZ mode in the Kretschmann configuration. The In:CuO film is 100 nm thick and has an electron concentration of $8.1 \times 10^{19}$ e-/cm$^3$. c) Reflectivity spectrum of a coupled PH-ENZ mode in the Kretschmann configuration, with the coupling point and Rabi splitting energy noted. The ENZ-on-SPP bilayer sample is 100 nm thick ENZ layer ($8.1 \times 10^{19}$ e-/cm$^3$) on top of a 300 nm thick SPP layer ($2.5 \times 10^{20}$ e-/cm$^3$). d) Theoretical dispersion curves of coupled upper/lower branches (thick blue/red lines) resulting from strong coupling between bare SPP/ENZ dispersion curves (dashed orange/green lines). e) Simulated (transfer matrix method) reflectivity map of the coupled ENZ-on-SPP bilayer. f) Simulated (finite integration technique) reflectivity map of the coupled ENZ-on-SPP bilayer. g) Calculated real and imaginary wavevectors of the experimental SPP dispersion in part (a), the experimental coupled modes in part (c), and the simulated coupled modes in part (e). Note: reflectivity maps plot R=Rp/Rs on the color axis, energy (wavenumbers) on the y-axis, and the film-parallel component of incident wavevector (normalized by $k_0 = \omega/c$) on the x-axis. See Fig. 5.7 for a comparison between angle, wavevector, and normalized wavevector for the dispersion relation plotted in part (c).
of the uncoupled ENZ mode, and $\omega_R$ is the Rabi splitting energy. This model is presented in Fig. 5.1d and quantitatively matches our experimental results remarkably well, giving strong evidence for a hybrid PH-ENZ mode formed through polaritonic strong coupling. Qualitatively, this behavior can be described as follows: distinct upper and lower branches (blue and red curves, respectively) result from this coupling, with Rabi splitting at the intersection of the bare SPP and bare ENZ dispersion curves (orange and green dashed curves, plotted for visual reference). At the coupling point, the UB (LB) is associated with a hybrid symmetric (antisymmetric) PH-ENZ mode that has both SPP and ENZ character. Far away from the coupling point, the UB and LB asymptotically approach the bare SPP and bare ENZ dispersion curves, respectively, and the mode profiles primarily adopt the behavior of the asymptote to which the branch is closest. More specifically, Rabi splitting requires the following inequality to be satisfied:\(^\text{127,129}\)

$$\omega_R > \frac{1}{2}(\gamma_{SPP} - \gamma_{ENZ})$$

where $\gamma_{SPP}$ and $\gamma_{ENZ}$ are the damping frequencies of the SPP and ENZ layers, respectively. Thus, it appears that using high mobility In:ZnO as the low-loss building blocks for our bilayers is an important prerequisite to the strong coupling we observe here. Note that the splitting energy is on the order of $(> 1/4)$ the uncoupled resonant energy at the coupling point, which may qualify this effect as ultrastrong coupling.\(^\text{127}\)

We are also able to accurately simulate the hybrid PH-ENZ mode of this same ENZ-on-SPP bilayer using two different computational methods, a MATLAB-based transfer matrix method (TMM, Fig. 5.1e) and a commercial finite integration technique (CST, Fig. 5.1f). Thanks to the excellent agreement between our simulations and experimental results, we are able to use simulations below to make inferences about the physical behavior of PH-ENZ modes in our bilayers, such as electric field profiles. To complete our analysis of this representative bilayer structure, we provide the imaginary wavevector of the coupled system (Fig. 5.1g), which is calculated at each frequency by fitting our data and the simulations (see SI and Fig. 5.8 for more detail). This is useful because Im($k_x/k_0$) can give us insight into the loss characteristics and propagation lengths of coupled PH-ENZ modes. Compared to the SPP reference calculations, we see that both Re($k_x/k_0$) and Im($k_x/k_0$) diverge strongly within the middle of the gap region at the ENZ frequency due to Rabi splitting arising from the modal strong coupling. At the edges of the gap region, close to the ENZ frequency, both Re($k_x/k_0$) and Im($k_x/k_0$) are larger for the symmetric/antisymmetric PH-ENZ mode than for the SPP mode due to the strong absorption and field confinement within the ENZ layer and associated

---

\(^a\) $\omega \approx \omega_p \left[1 - \frac{d}{\lambda^2} \right] - i \frac{\gamma}{2}$, where $d$ is the film thickness, after Ref. \(^[100]\)

\(^\text{ii}\) The spatial overlap between the ENZ and SPP electric fields: $\omega(r) = \int E_{ENZ}(r) \bullet E_{SPP}(r) dV$, (Ref. \(^[129]\)) here simply set to 717 cm\(^{-1}\)
optical losses. However, given that the modes still have a non-zero group velocity, PH-ENZ modes have non-negligible propagation lengths on the order of 5-10 $\mu$m, (see Fig. 5.8c) and which is about 30-60% of the SPP propagation length at the same frequencies. This ‘lossy’ propagation is ideal for integrating ENZ behavior within waveguide-based nanophotonics, which would be difficult to achieve using uncoupled ENZ modes.

To further understand the tunable behavior of PH-ENZ modes, we grew a number of ENZ-on-SPP bilayers with systematically decreasing carrier concentration in the 100 nm thick ENZ layer, effectively (de)tuning the SPP-ENZ interaction. Our experimental (top row) and calculated (bottom row) spectra are provided in Fig. 5.2 a-d and demonstrate that by changing the ENZ frequency of the top layer through carried density changes, that this strong coupling point is shifted within the dispersion relation. As expected, when the ENZ layer has higher electron concentration than the SPP layer, there is no spectral overlap between the ENZ and SPP dispersion relations and thus, little to no coupling results (Fig. 5.2a). As the carrier density decreases such that the ENZ condition approaches the asymptote of the SPP dispersion, which occurs in this system once the carrier concentration of the ENZ layer drops to $\sim1.5\times10^{20}$ e-/cm$^3$ (Fig. 5.2b), strong ENZ-SPP hybridization and coupling occurs. As the electron concentration continues to decrease, the coupling point moves to lower energy and lower wavevector (Fig. 5.2c,d). Additionally, the upper branch acquires greater dispersive character suggesting that the UB and LB are strongly coupled over a wider range of wavevectors.

A second critical element controlling coupling strength is the oscillator strength of the constituent modes. This can be readily tuned by changing the thickness of the ENZ layer at a constant carrier density-as the thickness changes, so will the magnitude of the electric field overlap integral that determines the Rabi splitting. For this experiment, we grew two additional ENZ-on-SPP bilayers, comparable to that in Fig. 5.2b: one with an 80 nm thick and another with a 20 nm thick ENZ layer, both with a carrier density of $1.5\times10^{20}$ e-/cm$^3$. Experimental dispersion relationships (Fig. 5.3 a and d) of these bilayers show a clear and systematic decrease in the Rabi splitting between the UB and LB as the ENZ layer thickness is reduced from 100 nm (Fig. 5.2b), to 80 nm (Fig. 5.3a) to 20 nm (Fig. 5.3d). Once again, both TMM (FFig. 5.3b,e) and CST simulations (Fig. 5.3c,f) model this behavior well.

By using CST to simulate the structure in the inset of Fig. 5.3d, we can visualize the mode/electric field profiles at discrete points labeled as a-f with asterisks in Fig. 5.3f along the UB and LB. These field profiles (electric field magnitude in the transverse/film normal/z-direction) are provided in Fig. 5.4 a-f, where each specific panel corresponds to the position in Fig. 5.3f of the same letter label. The corresponding longitudinal/x-direction electric field profiles can be found in Fig. 5.9a-f and Poynting vector fields are shown in the detail views of Fig. 5.4. We analyze this particular structure because the regions of the dispersion relationship where both the UB and LB exhibit evidence of strong coupling (Fig. 5.4b,e) are clearly delineated from the regions where the modes are uncoupled (Fig. 5.4a,d) and/or weakly coupled (Fig. 5.4c,f).
Figure 5.2 Tuning PH-ENZ modes by changing electron concentration in the ENZ layer. Top row: experimental IR reflectivity maps. Bottom row: TMM simulations. a) ENZ layer electron concentration: $3.5 \times 10^{20}$ e-/cm$^3$. b) ENZ layer electron concentration: $1.5 \times 10^{20}$ e-/cm$^3$. c) ENZ layer electron concentration: $9.5 \times 10^{19}$ e-/cm$^3$. d) ENZ layer electron concentration: $4.0 \times 10^{19}$ e-/cm$^3$. The ENZ layer is 100 nm thick. The SPP layer is 300 nm thick and has an electron concentration of $2.5 \times 10^{20}$ e-/cm$^3$. 
Figure 5.3 Tuning PH-ENZ modes in ENZ-on-SPP bilayers by changing ENZ layer thickness. a) Experimental IR reflectivity map of an ENZ-on-SPP bilayer with an 80 nm thick ENZ layer. Inset: geometry/electron concentration of the bilayer. b) Simulated (TMM) reflectivity map of the structure in the inset of (a). c) Simulated (CST) reflectivity map of the structure in the inset of (a). d) Experimental IR reflectivity map of an ENZ-on-SPP bilayer with a 20 nm thick ENZ layer. Inset: geometry/electron concentration of the bilayer. e) Simulated (TMM) reflectivity map of the structure in the inset of (a). f) Simulated (CST) reflectivity map of the structure in the inset of (a). The asterisks denote the points along the dispersion simulated in Fig. 5.4.
Figure 5.4 Electric field/mode profiles of the ENZ-on-SPP bilayer simulated in Fig. 5.3f (see structure in Fig. 5.3d).  

a) Uncoupled upper branch mode profile (point a in Fig. 5.3f) with predominant ENZ character. Detail view: Field confinement within the 20 nm ENZ layer with low propagation (Poynting vector field overlaid in all detail views).  
b) Strongly coupled upper branch PH-ENZ mode profile (point b in Fig. 5.3f) with hybrid ENZ-SPP behavior. Note that the field profile is symmetric/in phase. Detail view: Symmetric simultaneous field confinement within the ENZ layer and evanescent decay into the free space above with propagation in the ENZ layer and at the bilayer surface.  
c) Uncoupled upper branch mode profile (point c in Fig. 5.3f) with predominant SPP character. Detail view: Evanescent field decay into free space and into the bulk of the SPP layer with lowered propagation.  
d) Uncoupled lower branch mode profile (point d in Fig. 5.3f) with predominant SPP character. Detail view: Evanescent field decay into free space, with the propagating mode confined to the bilayer surface.  
e) Strongly coupled upper branch PH-ENZ mode profile (point e in Fig. 5.3f) with hybrid ENZ-SPP behavior. This field profile is antisymmetric/out of phase. Detail view: Antisymmetric simultaneous field confinement within the ENZ layer and evanescent decay into the free space above, with ENZ layer propagation in the opposite direction as at the bilayer surface.  
f) Uncoupled lower branch mode profile (point f in Fig. 5.3f) with predominant ENZ character. Detail view: Field confinement and low propagation within the 20 nm ENZ layer.
At low wavevectors (e.g., long polariton wavelength), the SPP and ENZ modes have sufficient spectral separation to eliminate any significant coupling between the modes. Thus, we anticipate that these positions along the UB (Fig. 5.4a) and LB (Fig. 5.4d) should largely resemble the uncoupled ENZ and SPP modes, respectively. Indeed, the electric fields in Fig. 5.4a are largely confined within the 20 nm thick ENZ layer, as in an uncoupled ENZ mode. Likewise, the Poynting vector field is largely confined to the ENZ layer and the magnitude of the energy flux is low. In contrast, the LB at this wavevector (Fig. 5.4d) exhibits an optical mode that is confined at the bilayer surface with electric fields that evanescently decay into the surrounding medium, indicative of an uncoupled SPP mode. For this SPP-like mode, the Poynting vector field is nearly completely isolated to the bilayer surface and the surrounding medium with correspondingly high propagation/energy flux.

As the two modes converge and reach the point where they would cross, a strong coupling occurs, resulting in the observed Rabi splitting of the two dispersion branches. At this coupling point (Fig. 5.4b,e for the UB and LB, respectively), we observe modal profiles that simultaneously resemble both ENZ and SPP modes. In the UB (Fig. 5.4b), we identify the PH-ENZ mode to have both strong field confinement within the ENZ layer and an intense evanescent decay into the surrounding medium. Because the UB is at higher energy, this is a symmetric PH-ENZ mode, with the evanescent fields and ENZ-confined fields approximately in phase. The Poynting vector field also takes on a new profile, as the energy flux is distributed throughout the ENZ layer and surrounding medium, and, to a small extent, the SPP layer. Importantly, the energy flux is strongest within the ENZ layer itself and the maximum Poynting vector magnitude is more than three times greater than in the ENZ-like mode (Fig. 4a). We calculate propagation lengths on the order of 5μm (Fig. 5.8) for this coupled PH-ENZ mode in the upper branch, thanks to the fact that the electric fields are no longer entirely confined to the ENZ layer. The lower branch (Fig. 5.4e) contains the anti-symmetric PH-ENZ mode, which again exhibits simultaneously strong evanescent fields and field confinement within the ENZ layer, but with the fields in the two layers out of phase. Here, the energy flux is again mostly in the ENZ layer but propagates in the opposite direction within this layer. Thanks to the larger Poynting vector magnitude, propagation distances are higher for this anti-symmetric PH-ENZ mode (Fig. 5.8).

Finally, at wavevectors well above the strong coupling point (Fig. 5.4c,f), the UB, which initially began with ENZ character, transitions to primarily SPP-like behavior (Fig. 5.4c), while the opposite is observed in the LB (original SPP character transitions to ENZ behavior with limited power propagation; Fig. 5.4f). Interestingly, the UB at high wavevectors exhibits electric field decay into the CdO SPP layer and substrate (Fig. 5.4c), which we attribute to the In:CdO SPP layer having a negative but small real part of the dielectric function. Because of the low carrier densities (relative to metals) employed here, this leads to a skin depth of CdO at these frequencies that is on the order of hundreds of nanometers to microns, so the SPP-like mode can decay into both the dielectric ambient as well as into the CdO film itself.

We conclude our investigation with additional TMM simulations to more thoroughly characterize
how the tuning parameters influence coupling and Rabi splitting in ENZ-on-SPP bilayers. To do so, we simulate the reflectivity spectra for bilayers with varying ENZ layer carrier concentration and thickness and determine the Rabi splitting by finding the smallest UB/LB peak separation in the reflectivity map for each simulated stack. Fig. 5.5a displays the results of this analysis, with the Rabi splitting plotted against the detuning energy (i.e., the difference in plasma frequency between the SPP and ENZ layers) for a number of ENZ layer thicknesses. Two trends are immediately apparent. First, the Rabi splitting is maximized at detuning energies ranging from 2000-4000 cm$^{-1}$, which corresponds to ENZ layer carrier concentrations of 1-1.5×10$^{20}$ e-/cm$^3$. As seen in our prior results discussed above, this detuning energy corresponds to the strongest overlap of the bare ENZ and bare SPP dispersion curves (SPP layer: 2.5×10$^{20}$ e-/cm$^3$, 300 nm). The slight shift of the Rabi splitting maximum to higher detuning energies with ENZ layer thickness is likely the result of the increasing thickness increasing the effective dielectric constant seen by the SPP layer, which suppresses the bare SPP dispersion curve and requires a slightly lower ENZ layer carrier concentration for maximum overlap. The second clear trend is that the Rabi splitting monotonically and categorically increases with ENZ layer thickness (oscillator strength), as predicted (Fig. 5.5b). Note that this trend does not continue indefinitely but rather plateaus, which is due to the fact that thicker films lose the ability to sustain ENZ modes.

5.1.3 Conclusion

Here, we have demonstrated that ENZ-on-SPP coupling within bilayer In:CdO structures exhibit (ultra)strong coupling, characterized by Rabi splitting energies as large as 1/4 to 1/3 of the incident field energy. The resulting hybrid SPP-ENZ modes, or PH-ENZ modes, are highly tunable through changes in the ENZ layer thickness (oscillator strength) and the carrier concentration of the ENZ/SPP layer (spectral overlap between the two modes). Furthermore, PH-ENZ modes combine the attractive features of SPP and ENZ modes by simultaneously achieving increased group velocity and electric field confinement within the bilayer. We believe that tunable, coupled PH-ENZ modes will be particularly attractive for applications in IR nanophotonic circuitry and waveguides, where simultaneous field confinement and mode propagation around uneven shapes and sharp corners is desirable. Related additional potential applications for strongly coupled PH-ENZ modes may include quantum information processing or thresholdless lasing.$^{127,131,132}$ Finally, the resonant absorption properties of these structures may also be highly useful for surface enhanced infrared sensing applications or catalysis,$^{133,134,135}$ as the tunable nature of PH-ENZ modes offers the opportunity to tailor the modal energies and dispersion to resonate with specific electronic levels or vibrational states. Combined with the ease with which bilayers are fabricated, we expect PH-ENZ modes to quickly find applications in one or more of these areas.
Figure 5.5 TMM simulations of coupling and Rabi splitting for a wide range of ENZ layer electron concentration and ENZ layer thickness. 

a) PH-ENZ mode Rabi splitting vs. detuning energy, which is defined as the difference between the SPP layer’s plasma frequency and the ENZ layer’s plasma frequency. Experimental results (filled circles) for ENZ-on-SPP bilayers with 100 nm thick ENZ layers are included for comparison.

b) PH-ENZ mode Rabi splitting vs. ENZ layer thickness. The ENZ carrier concentration is set at $1.5 \times 10^{20} \text{e}^-/\text{cm}^3$. Experimental results (filled circles) are included for comparison.
5.1.4 Experimental

Extensive descriptions of our methods for depositing doped CdO thin films can be found in the Supporting Information. Briefly, we deposit heteroepitaxial CdO onto epi-ready double side polished r-plane sapphire using reactive high-power impulse magnetron sputtering (R-HiPIMS) from a 99.9999% pure metallic Cd target. Doping is achieved by RF co-sputtering from a 99.99% pure metallic In target. Thickness/deposition rate and carrier concentration are calibrated using x-ray reflectivity and Hall effect measurements, respectively. To form doped CdO bilayers, we first deposit 300 nm In:CdO (the SPP layer) with an electron concentration of $2.5 \times 10^{20}$ e-/cm$^3$. After a 2 minute rest without breaking vacuum, a homoepitaxial In:CdO layer (the ENZ layer) is deposited on top of the SPP layer. The electron concentration and thickness of the ENZ layer are controlled by the RF power applied to the In target and the deposition time, respectively. Post-deposition, the bilayers are annealed at 700$^\circ$C in pure oxygen for 30 minutes. X-ray diffraction confirms that the ENZ-on-SPP bilayers are homo-/heteroepitaxial, and secondary ion mass spectroscopy confirms that the In$^{3+}$ donors are localized to the SPP and ENZ layers in different concentrations, as expected.

Optical properties (polarized reflectivity spectra) were characterized using a Woollam IR-VASE ellipsometer. A 90$^\circ$ calcium fluoride (CaF$_2$) prism and n=1.720 index matching fluid were used to couple IR light into our plasmonic films through the polished substrate in the Kretschmann-Raether configuration. All reflectivity data were recorded with p- and s-polarized light and are plotted using $R=rp/rs$ as the color/z-coordinate, energy (in cm$^{-1}$) as the y-coordinate, and normalized wavevector as the x-coordinate ($k_x/k_0$, unitless, where $k_x$ is the component of the incident light wavevector parallel to the film surface, and $k_0=\frac{\omega}{c}$).

To simulate the optical response of our bilayer films, we use a combination of the transfer matrix model (TMM) and the CST Studio software. Our TMM model is based on a homebuilt Matlab code that includes frequency-dependent dielectric dispersions for CaF$_2$ and sapphire and generates frequency-dependent dielectric functions for each plasmonic layer based on the Drude model. This provides a computationally-inexpensive method to simulate the reflectivity spectra of our coupled bilayers. The CST software solves Maxwell’s equations based on the finite integration technique (FIT), allowing us to simulate electric field profiles in addition to reflectivity spectra.

5.1.5 Supplementary Information

**In:CdO bilayer growth:** Indium doped cadmium oxide (In:CdO) is grown using RF-assisted reactive high power impulse magnetron sputtering (R-HiPIMS). Cd is sputtered from a circular 2-inch metallic Cd target (99.9999%, Osaka Asahi Metal), which is pressed and cut in-house and mounted to a MeiVac MAK 2 inch magnetron sputtering source. In is sputtered from a circular 1-inch metallic In target (99.99%, Sigma Aldrich), which is pressed and cut in-house and mounted to an AJA 1 inch magnetron sputtering source. The sputtering sources are housed in a high-vacuum sputtering
system with a turbomolecular pump with a base pressure of $10^{-7}$ Torr. All films are deposited in a combined Ar-O$_2$ atmosphere at 10 mTorr, which is achieved by flowing 19 sccm Ar and 15 sccm O$_2$ into the vacuum chamber using mass flow controllers and by adjusting a gate valve between the vacuum chamber and the pump.

Power is delivered to the Cd target using an Advanced Energy MDX 1.5K DC power supply in concert with a Starfire Industries Impulse Pulsed Power Module. The DC supply is run in constant voltage mode to deliver approximately 420 V to the HiPIMS pulse generator. The HiPIMS pulsed deposition parameters are kept constant at 80 $\mu$s pulse width and 800 Hz repetition rate, which corresponds to a 1250 $\mu$s pulse period and a 6.4% sputtering duty cycle. This gives a deposition rate of about 25 nm/minute. Doping is achieved by applying RF power to the In target using Advanced Energy RFX-600 RF power supply with a Manitou Systems manual matching network. Film thickness is controlled by deposition time, while dopant/carrier concentration is controlled by changing the RF power applied to the In target (between 2.4 W/cm$^2$ to 7.9 W/cm$^2$).

All ENZ-on-SPP bilayer samples described in the main text are fabricated by first depositing a 300 nm In:CdO layer (the SPP layer) on double-polished epi-ready r-plane sapphire (Jiaozuo TreTrt Materials) affixed to a stainless steel puck with silver paint (Ted Pella). The puck and substrate are heated to a deposition temperature of 370°C as measured using a Raytek 1.6 $\mu$m MM Series Pyrometer. In every case, this SPP layer is grown using 6.1 W/cm$^2$ of RF power density on the In target to achieve carrier concentrations of $2.5\times10^{20}$ e-/cm$^3$. The bilayer is completed by growing an additional homoepitaxial layer (the ENZ layer), on top of the SPP layer, with controlled thickness and carrier concentration. Between the SPP layer deposition and subsequent ENZ layer deposition, the substrate is shuttered for 5 minutes while the In target power is adjusted as desired. This rest helps improve reproducibility in deposition rate and carrier concentration in our bilayers. Following deposition, all samples are annealed at 700°C in pure O$_2$ for 30 minutes.

**Characterization:** Structural properties (thickness, crystallinity, etc.) of our samples are measured by X-ray diffraction using a PANalytical Empyrean X-ray diffractometer in parallel beam geometry (double-bounce hybrid monochromator incident optic, parallel plate collimator receiving optic). Reciprocal space maps are collected using a PANalytical PIXcel area detector. In:CdO electronic properties (carrier concentration, mobility) are measured by the Hall Effect using an Ecopia HMS-3000 system with a 0.51 T magnet. Dopant depth profiles are characterized with time-of-flight secondary ion mass spectroscopy (ToF-SIMS) using an ION-TOF TOF-SIMS V instrument with a cesium source for sputtering and a bismuth liquid metal ion gun (SMIG) source in interlaces sputtering mode for analysis. For depth profiles, a Cs$^+$ sputtering beam with 10 keV energy and 25 nA current is rastered over a 120x120 $\mu$m area. The Bi$^{3+}$ analysis beam is 0.4 pA at 25 keV and rastered over a 50x50 $\mu$m area at the center of the sputtered crater. The angle of incidence is 45° from normal for both beams.

The plasmonic response of the bilayers is measured with infrared polarized reflectivity spec-
Figure 5.6 Structural characterization of a representative In:CdO ENZ-on-SPP bilayer. (a) Reciprocal space map showing heteroepitaxy between CdO and the r-plane sapphire substrate. The discrete CdO (002) and (113) peaks also indicate that the ENZ layer is homoepitaxial with respect to the SPP layer beneath it. (b) Rocking curves of the CdO (002) and (111) reflections, and the r-plane sapphire reflection. The low peak widths for CdO are an indication of high quality films and hetero-/homoepitaxy. (c) Skew-symmetric 360° ω̂ θ̂ scan about the CdO (111) reflection (ω: 54.7°, 2θ: 33°). The four-fold symmetry confirms hetero-/homoepitaxy. (d) ToF-SIMS spectra showing the depth profile of Cd and In in the bilayer film (left: bilayer surface right: substrate). The InO⁻ signal confirms distinct dopant concentrations in the ENZ and SPP layers.
troscopy using a Woollam IR-VASE ellipsometer. A 90° calcium fluoride (CaF2, Thor Laboratories) prism, n=1.720 index matching fluid (Cargille Series M), and a home-built aluminum sample holder are used to couple IR light into the samples through the back side of the polished substrate in the Kretschmann-Raether configuration. The silver paint is removed from the backside of the substrate with a razor blade and/or sandpaper prior to optical measurements. For each sample, the reflectivity of both p- and s-polarized light reflectivity are collected as a function of incident light energy and ellipsometer angle (Fig. 5.7a). The dispersion relationships are plotted using $R = r_p/r_s$ as the reflectivity/color/z-coordinate, which provides self-consistent backgrounding. Energy (in cm$^{-1}$) as is plotted as the y-coordinate, and normalized wavevector is plotted as the x-coordinate ($k_x/k_0$, unitless, where $k_x$ is the component of the incident light wavevector parallel to the film surface, and $k_0=\nu_0\lambda_0/c$). To convert from ellipsometer angle to $k_x/k_0$ (Fig. 5.7b), a MATLAB script is used to interpolate the data over the consistent range $1<k_x/k_0<1.3$ at each individual ellipsometer angle and incident light energy, taking into account changes in incident angle and momentum due to the dispersive prism and substrate. The data are presented this way in the main text for easier visual interpretation over the un-normalized $k_x$ (Fig. 5.7c).

Calculation of complex wavevector: To extract the imaginary part of the wavevector in Fig. 5.1g of the main text, the reflectivity minimum as a function of wavevector is fitted to a negative Lorentzian peak at each individual frequency using a nonlinear curve fit algorithm in MATLAB. To achieve better fits, a linear background component ($R_0-R_1 k$) is added to the fitting function, which is:

$$R(k) = R_0 - R_1 k - A \frac{\Gamma^2}{(k-k_0)^2 + \Gamma^2}$$

(5.3)

Where $R_0$ and $R_1$, and $A$ are constants. The fitted Lorentzian line width $\Gamma$ corresponds to the
Figure 5.8 Calculation of imaginary component of wavevector. (a) Fitted real component of wavevec-
tor ($k_0$, blue line) overlaid on the experimentally-measured PH-ENZ dispersion relation from Fig. 5.1c
of the main text. (b) Magnitudes of the real and imaginary components of the wavevectors for the
experimentally-measured PH-ENZ dispersion relation (thick solid line), the TMM-simulated PH-ENZ dis-
persion relation (thin solid line), and the experimentally-measured SPP dispersion relation from Fig. 5.1a
of the main text (thin dashed line). (c) Propagation lengths as calculated using the imaginary component
of the wavevector in part (b).

imaginary component of the wavevector, while the peak location $k_0$ gives the real component. Given
a good agreement between $k_0$ and the experimental/simulated dispersion (Fig. 5.8a), propagation
lengths can then be calculated as:

$$\frac{1}{2Im(k_x)}$$  \hspace{1cm} (5.4)

**TMM simulations:** The transfer matrix method is used to simulate the polarized reflectivity of our
samples at each discrete incident angle and energy. The transfer matrix allows us to solve Fres-
nelâ’Äôs equations for the multi-layered stacks examined in this study (i.e., prism//substrate//SPP
layer//ENZ layer//air) by taking advantage of the fact that the boundary conditions must be con-
tinuous across each interface. We use the following transfer matrices for p- and s-polarized light,
respectively, moving from layer $a$ to layer $b$:

$$T^p_{a\rightarrow b} = \frac{1}{2} \begin{pmatrix}
1+C_1C_2 & 1-C_1C_2 \\
1-C_1C_2 & 1+C_1C_2
\end{pmatrix}$$

$$T^s_{a\rightarrow b} = \frac{1}{2} \begin{pmatrix}
1+C_1^{-1}C_2 & 1-C_1^{-1}C_2 \\
1-C_1^{-1}C_2 & 1+C_1^{-1}C_2
\end{pmatrix}$$

$$C_1 = \sqrt{\frac{\varepsilon_a}{\varepsilon_b}}; \quad C_2 = \frac{\cos(\theta_b)}{\cos(\theta_a)}$$

where $\varepsilon_a(\omega)$ is the dispersive dielectric function of layer $a$, $\varepsilon_b(\omega)$ is the dispersive dielectric function

of the subsequent layer $b = a + 1$, and $\theta$ is the incident light angle in layer $a$ or $b$ (corrected for the prism angle, refraction, etc.). We use experimentally-determined dispersive dielectric functions for the CaF$_2$ prism and the sapphire substrate. For plasmonic In: CdO layers, the dispersive dielectric function is simulated using the Drude model:

$$
\epsilon_{In: CdO} = \epsilon_\infty - \frac{\omega_p^2}{\omega^2 - i\gamma \omega}
$$

$$
\omega_p^2 = \frac{n e^2}{\epsilon_0 m_e^*}
$$

$$
\gamma = \frac{e \mu}{m_e^*}
$$

where $\epsilon_\infty$ is the high-frequency dielectric constant, $\omega_p$ is the plasma frequency, $n$ is the electron concentration, $e$ is the charge of an electron, $\epsilon_0$ is the vacuum permittivity, $m_e^*$ is the effective mass of an electron, $\gamma$ is the damping frequency, and $\mu$ is mobility.

The propagation matrix for light moving through phase $a$ is:

$$
P_a = \begin{pmatrix}
e^{i k d_a} & 0 \\
0 & e^{-i k d_a}
\end{pmatrix}
$$

$$
k = \frac{\omega}{c} \sqrt{\epsilon_a \cos(\theta_a)}
$$

where $d_a$ is the thickness of layer $a$. The total product matrix is the sequence product of the transfer and propagation matrices over all layers:

$$
M_{pol.} = \prod_{layer \ n} T_{n-1 \to n}^{pol.} P_n T_{n \to n+1}^{pol.}
$$

The reflectivity coefficient and total reflectivity for a given polarization can be found from the product matrix by:

$$
r_{pol.} = \frac{m_{21}}{m_{11}}
$$

$$
R_{pol.} = |r|^2
$$

Thus, the transfer matrix method allows us to accurately simulate $R_p/R_s$ reflectivity maps for our bilayer samples over a discrete range of incident angles and frequencies. The TMM simulation
CST simulations: Full numerical simulations of the electromagnetic field are conducted using the frequency domain solver CST Studio suite 2017. Plane waves were used to excite a 4µm by 4µm unit cell, consisting of a calcium fluoride background, a sapphire substrate (1µm), doped CdO layers (as experiment), and then a vacuum spacer (7.5µm). The compressed substrate layers ensure accurate in-plane wavevectors without excessive computational cost. Reflectivity maps are produced by varying incident angle (θ), and then converting to wavevector as described above. Two-dimensional field profiles were extracted from the center of the simulation at the particular frequencies and angles described in the main text.
Chapter 6

Conclusions and Future Work

The work presented in this dissertation provides an alternative low loss tunable plasmonic material in the mid-IR where unprecedented phenomena can be investigated. Further, the mode mixing capabilities discussed in the later chapters demonstrates the potential photonic applications of doped cadmium oxide.

6.0.1 Conclusion

6.0.1.1 Doped Cadmium Oxide

Here, we have demonstrated that doping cadmium oxide with acceptors and donors allows for the carrier concentration to be tuned from $5 \times 10^{18}$ cm$^{-3}$ to $5 \times 10^{20}$ cm$^{-3}$. In all cases, mobilities were measured to be greater than 200 cm$^2$/Vs, proving doped cadmium oxide to be a low loss plasmonic material.

All of the dopants reported provide some insight into the dopant requirements for maintaining high mobility cadmium oxide. The following serves to highlight some of the most distinct observations:

1. Dysprosium confirmed sputtering to be a feasible alternative to MBE, which was a great accomplishment that allowed high throughput experiments.

2. Aluminum placed a lower limit on the ionic radius needed to achieve high mobility cadmium oxide (although 300 cm$^2$/Vs is still relatively high).

3. Yttrium provided us with an additional dopant that gives rise to a peak in mobility that is actually higher than dysprosium.

4. Silver allowed cadmium oxide to be acceptor doped to lower carrier concentrations.
5. Indium proved to be the most promising dopant. It enabled mobilities comparable to yttrium with carrier concentration that extend into the mid-$10^{20}$'s.

6. Cerium and tin were used in an attempt to achieve carrier concentrations in the $10^{21}$'s, but were ultimately limited to the mid to low $10^{20}$'s.

In addition, as the dissertation progressed, the synthesis method was further developed. Beginning with RF co-sputtering, dysprosium, yttrium, and aluminum doping were successfully demonstrated. But, there were several disadvantages—sputtering target poisoning, slow sputter rates (comparable to MBE), and unwanted anion sputtering. To overcome these disadvantages, we implemented an alternative deposition technique, high-power impulse magnetron sputtering (HiPIMS) which is a subset of pulsed DC sputtering. This resulted in much higher sputter rates and reproducible film quality. Moving forward using HiPIMS, yttrium, silver, cerium, tin, and indium were explored as dopants. Altogether, we identified several promising dopants and two alternative growth techniques for doped cadmium oxide.

6.0.1.2 Transfer Matrix Method Modeling

The transfer matrix method reflectivity simulation is an essential tool for determining the appropriate cadmium oxide properties for tailored plasmon polariton coupling. By assuming cadmium oxide to be a Drude metal, the transfer matrix method model captures the plasmonic response as a function of effective mass, high frequency dielectric constant, mobility, carrier concentration, and thickness, all of which can change a function of doping.

In addition to accurately modeling single plasmonic layers, it can be extended to multilayer structures, which was the focus of the last two chapters. Altogether, the transfer matrix method is truly beautiful due to its simplicity, speed, and accuracy (at least for the CdO material system). Not only has it provided a road-map for designing cadmium oxide thin films, it has assisted in determining desired material properties for future materials development.

6.0.1.3 Cadmium Oxide Homostructures

In this study, we successfully grew cadmium oxide homostructures with different carrier concentrations and thicknesses to achieve multi-spectral ENZ plasmonic coupling. Using the advantageous HiPIMS method, an electronic interface without the presence of a structural interface was achieved, fabricating a monolithic low loss system. The work presented here demonstrates the capabilities of doped cadmium oxide synthesized via HiPIMS. Structures similar to these could allow for devices, such as detectors and energy harvestors, in the mid-IR to be created in a monolithic fashion unlike current methods.
6.0.1.4 Multiple Mode Interactions in Doped CdO Thin Films

Currently in the plasmonics and photonics community, the need to design the optical dispersion of thin films is of high importance. Engineering the optical dispersion of a thin film would allow for unprecedented light-matter interactions capable of steering the future of optics. As such, understanding how various plasmonic modes in a given system, which can significantly alter the optical dispersion, interact with each other is the first step in achieving a completely engineered dispersion. In this work, we have identified the extent to which an ENZ and SPP mode interact in the mid-IR using the doped cadmium oxide system. Through thoroughly investigating the mode splitting, or Rabi splitting, as a function of tuning and detuning of the resonant energies, we were able to assess the optimal conditions for creating a hybrid mode, termed PH-ENZ mode. Furthermore, we have demonstrated that the PH-ENZ mode allows for joint characteristics of ENZ and SPP modes- high electric field confinement and mode propagation. It is important to note that although the coupling of these modes is fairly complex, the details of the coupling are still captured in the transfer matrix method simulation.

6.0.2 Future Work

The purpose of this section is to provide additional ideas and applications of doped cadmium oxide. As this dissertation is coming to an end, there are several projects that I did not get to fully pursue. Thus, I have included them in this section.

6.0.2.1 Epsilon-Near-Zero Mode Interaction in Multilayer Homoeptaxial Structures

Extending the previous conversation of coupled modes, an ENZ-ENZ system has the ability to couple modes as well. If the two resonators can be spatially brought close together, there should be an ‘optimal’ separation distance that is dependent on the dielectric properties of the separating medium. In other words, if the electric fields of the two ENZ modes are able to interact, a mode splitting feature should be observable. To test this hypothesis, multiple five layer structures were fabricated illustrated in the bottom right panel of Fig. 6.1. The multilayer systems are comprised of (in the following order from substrate to surface): 100 nm intrinsic CdO, 50 nm of CdO doped to $2.5 \times 10^{20} \text{cm}^{-3}$, variable thickness of intrinsic CdO, 50 nm of CdO doped to $2.5 \times 10^{20} \text{cm}^{-3}$, and 100 nm intrinsic CdO. The purpose of 100 nm intrinsic CdO layers surrounding the system is to minimize interfacial defects causing the carrier concentrations of the two ENZ layers to be different. To vary the spatial separation of the ENZ modes, the thickness of the center intrinsic CdO layer was varied from 20 nm to 320 nm. The resulting reflectivity maps are presented in the top panels of Fig. 6.1. As the distance between the ENZ layers is increased, the ENZ mode splits into an upper branch and lower branch. Qualitatively, this mode splitting is extremely similar to the PH-ENZ mode where the modes split leaving a transparency window between the branches.
Figure 6.1 High resolution X-ray diffraction. Left) Two-theta Omega scans and Right) Omega scans of tin, indium, and cerium doped cadmium oxide at similar carrier concentrations.

To accompany the measured reflectivity, transfer matrix method (TMM) simulations are presented in the bottom panels of Fig. 6.1. Qualitatively speaking, the mode splitting shape is accurately captured in the simulation. In the 160 nm and 320 nm ENZ separation systems, the TMM simulation predicts a larger degree of absorption in the ENZ dispersions (compared to measured). Currently, the origin of different absorption values is unknown. It is certainly plausible that the material parameters in a multilayer sample could differ from the individual films, producing this observation.

Regardless of the difference in measured and simulation, two absorption branches can be observed in the previous discussion. Further understanding of the ENZ-ENZ mode splitting has potential in developing hyperbolic metamaterials and, more generally speaking, tailoring light-matter interactions.

When engineering doped cadmium oxide thin films for maximum absorption, in SPP and ENZ modes, the thickness is a critical component. As previously discussed, the thickness of thin film, relative to the skin depth, determines the plasmonic mode of the system. Further, for the ENZ modes with carrier concentrations greater than $7 \times 10^{19} \text{cm}^{-3}$, the thickness needs to be on the order 10's of nanometers. Fig. 6.2 shows the results of an intrinsic CdO thickness series grown on c-plane sapphire and MgO. As the thickness is decreased from 100 nm to 10 nm on both substrates, the carrier concentration decreases almost an order of magnitude. It is important to note that the mobility is decreasing as well, which implies, on a per volume (cm$^{-3}$) basis, the number of defects or scattering centers are increasing.

The carrier concentration's dependence on thin film thickness suggests evidence of Fermi
CdO Thickness Dependence: Fermi Level Pinning

Figure 6.2 Carrier concentration (black) and electron mobility (red) as a function of thickness for intrinsic (non-doped) CdO grown on c-plane sapphire (left) and MgO (right).

level pinning. Fermi level pinning (or Fermi stabilization energy) is a phenomenon present at semiconductor interfaces where the Fermi level is locked at a specific energy level. Depending on where the bulk Fermi level lies, the surface will electronically compensate via mechanisms such as vacancies (i.e. a large density of surface states). The effect has been observed in common material systems such as InN\textsuperscript{136}, GaN\textsuperscript{92,90}, Si\textsuperscript{137}, and Ge\textsuperscript{138}. In addition, this effect has been theoretically studied\textsuperscript{139,140}. In doped cadmium oxide, we believe the Fermi level is pinned approximately 1 eV (Chapter 3) above the conduction band minimum; thus, as the bulk Fermi level is pushed above and below the stabilization energy, we hypothesize compensating mechanisms such as cadmium and oxygen vacancies, respectively, are induced into the system. This effect can be seen in Fig. 6.2. As the thickness of the cadmium oxide thin film is decreased, the percent of the carrier concentration that the surface states are contributing to the total carrier concentration becomes larger. Therefore, a large increase in carrier concentration can be observed. The idea of interface defects, i.e. oxygen vacancies, being the root cause of this carrier concentration thickness dependence is further supported by a decrease in mobility (increased electron scattering centers).

One proposed method to determine if interface defects, or Fermi level pinning, are the origin of this thickness dependence is illustrated in Fig. 6.3. Fig. 6.3 shows reflectivity measurements of p-polarized/s-polarized light for two systems: a homoepitaxial structure where a low yttrium-doped cadmium oxide layer is surrounded by 100 nm intrinsic CdO, and a single low yttrium-doped cadmium oxide layer (both doped layers have the same amount of yttrium content). It is important to remember that at these thickness, an ENZ mode exits; thus, we can use the plasmonic absorption
as a metric for determining the change in carrier concentration. In both systems, the thickness of the yttrium-doped layer is 30 nm, 50 nm, and 70 nm for the red, green, and blue curves (respectively). For the single low yttrium-doped cadmium oxide system, a substantial decrease in absorption energy can be observed. Qualitatively, this decrease in absorption energy is due to a decrease in carrier concentration (or carrier density) in the yttrium-doped layer as the thickness is increased. In addition, the absorption energy (or carrier concentration/density) for the homoepitaxial system seems to stay relatively constant with increasing thickness indicating the intrinsic layers mitigate or eliminate the effects of Fermi level pinning, as expected.

In this work, we have demonstrated the effects of Fermi level pinning, and a successful method to reduce or eliminate this effect. Further work still has to be done to accurate determine the origins of this effect (e.g. highly doped thickness series and x-ray photoelectron spectroscopy).

### 6.0.2.3 Plasmonic Thermocouple

The Seebeck effect is a phenomenon in which a small voltage on the order of microvolts is measure between two dissimilar materials. Upon heating the junction, assuming the contact positions are at the same temperature, an increase in internal potential can be observed. This effect is ultimately the foundation of current thermocouples. Fig. 6.4 (left) illustrates a simple setup to integrate plasmonic heating with the Seebeck effect. Essentially, a junction is formed between intrinsic cadmium oxide and cadmium oxide doped to $7 \times 10^{19} \text{cm}^{-3}$, which corresponds to approximately 4 $\mu$m IR radiation.
A gold mirror is placed in two locations: at the top of the junction and on the back side of the substrate. The purpose of the gold mirror on the back side of the substrate is to selectively illuminate the junction, and minimize the possibility of illuminating the contact position (black hemispheres). The gold mirror on the top of the CdO layers is so an IR absorbing plasmonic mode (i.e. Brewster mode\textsuperscript{141}) can be accessed. Upon absorbing the p-polarized (same as previous discussions), the hot electrons will dissipate their energy into heat resulting in a temperature increase of the intrinsic cadmium oxide - doped cadmium oxide junction. Thus, an increase in the electromagnetic force (or voltage because $E=-\nabla V$) can be measured. This effect is illustrated in the right panel of Fig. 6.4.

As p-polarized IR light radiates the junction, an increase of approximately 40 $\mu V$ can be observed. Conversely, illuminating the junction with s-polarized light results in a small, approximately 15 $\mu V$ increase. As of now, we are uncertain of the mechanism causing an increase in voltage from s-polarized light.

The results shown in Fig. 6.4 are preliminary and need additional studies. For example, developing a thermopile comprised of the previous device will allow for significantly larger voltages to measured. In addition, these voltages were made using a Keithley electrical measurement stage. Significant alterations to the measurement setup would allow for an appreciable decrease in signal to noise (e.g. a lock-in amplifier).

**Figure 6.4** Left) Illustration of plasmonic thermocouple comprised of an intrinsic and yttrium-doped cadmium oxide layer with a carrier concentration of $7 \times 10^{19}$ cm$^{-3}$, and gold mirrors (yellow layers) to restrict illumination to the interface between the two CdO layers. EMF with black semicircles signifies the location of voltage measurements. Right) Electromagnetic Force ($\mu V$) as a function of time seconds as the CdO layers are illuminated with p-polarized and s-polarized light.
6.0.2.4 Broadband Absorber

A broadband absorber in the mid-IR has many applications in energy harvesting, thermal cloaking, and detectors (previous section). By growing homoepitaxial layers of doped CdO with small increases in the dopant concentration, or carrier concentration, a broadband absorber was fabricated (Fig. 6.5). In Fig. 6.5, the left panel shows the reflectivity map (p-polarized/s-polarized) as a function of angle for a seven layer ENZ system and the right panel shows a line scan of the reflectivity map at 51°. At 51°, the broadest range of energies for absorption was achieved. It is clear that optimization of the carrier concentration from layer to layer will lead to an improved broadband absorber. However, these preliminary results provide a foundation for the fabrication of a broadband absorber, and the realization of other devices, such as a optical notch filters.

![Figure 6.5](image-url)

**Figure 6.5** Left) Reflectivity map in Kretschmann configuration of a seven layer ENZ homostructure. Right) Line scan of reflectivity map at an incident angle of 51°.


Appendix A

Electrical Properties
A.1 High Power Impulse Magnetron Sputtering

Figure A.1 Carrier concentration and mobility as a function of power density per working distance (proportional to flux) for unannealed and annealed state of cerium doped cadmium oxide grown on c-plane sapphire via HiPIMS.
Figure A.2 Carrier concentration and mobility as a function of power density per working distance (proportional to flux) for unannealed and annealed state of indium doped cadmium oxide grown on c-plane sapphire via HiPIMS.
Figure A.3 Carrier concentration and mobility as a function of power density per working distance (proportional to flux) for unannealed and annealed state of tin doped cadmium oxide grown on c-plane sapphire via HiPIMS.
Figure A.4 Carrier concentration and mobility as a function of power density per working distance (proportional to flux) for unannealed and annealed state of yttrium doped cadmium oxide grown on c-plane sapphire via HiPIMS.
Figure A.5 Carrier concentration and mobility as a function of power density per working distance (proportional to flux) for unannealed and annealed state of silver doped cadmium oxide grown on MgO via HiPIMS.
Figure A.6 Carrier concentration and mobility as a function of power density per working distance (proportionional to flux) for unannealed and annealed state of cerium doped cadmium oxide grown on MgO via HiPIMS.
Figure A.7 Carrier concentration and mobility as a function of power density per working distance (proportional to flux) for unannealed and annealed state of indium doped cadmium oxide grown on MgO via HiPIMS.
Figure A.8 Carrier concentration and mobility as a function of power density per working distance (proportional to flux) for unannealed and annealed state of tin doped cadmium oxide grown on MgO via HiPIMS.
A.2 Radio Frequency Sputtering

Figure A.9 Carrier concentration and mobility as a function of power density per working distance (proportional to flux) for annealed state of aluminum doped cadmium oxide grown on c-plane sapphire via RF sputtering.
Figure A.10 Carrier concentration and mobility as a function of power density per working distance (proportional to flux) for unannealed and annealed state of dysprosium doped cadmium oxide grown on c-plane sapphire via RF sputtering.
Figure A.11 Carrier concentration and mobility as a function of power density per working distance (proportional to flux) for annealed state of yttrium doped cadmium oxide grown on c-plane sapphire via RF sputtering.
Figure A.12 Carrier concentration and mobility as a function of power density per working distance (proportional to flux) for annealed state of yttrium doped cadmium oxide grown on MgO via RF sputtering.
A.3 CdO Electrical Properties Thickness Dependence

Figure A.13 Carrier concentration and mobility as a function of thickness for annealed and unannealed intrinsic cadmium oxide grown on MgO.
Figure A.14 Carrier concentration and mobility as a function of thickness for annealed and unannealed intrinsic cadmium oxide grown on Si.
Figure A.15 Carrier concentration and mobility as a function of thickness for annealed and unannealed intrinsic cadmium oxide grown on c-plane $\text{Al}_2\text{O}_3$. 
A.4 Process Parameters

Figure A.16 Carrier concentration and mobility as a function of deposition temperature measured via pyrometer for unannealed and annealed yttrium doped cadmium oxide at approximately 150 nm on c-plane sapphire.
Figure A.17 Carrier concentration and mobility as a function of deposition temperature measured via pyrometer for unannealed and annealed intrinsic cadmium oxide at approximately 150 nm on c-plane sapphire.
Figure A.18 Carrier concentration and mobility as a function of anneal time in minutes for intrinsic cadmium oxide grown on c-Al$_2$O$_3$. Annealed at 700°C in O$_2$. 
Figure A.19 Carrier concentration and mobility as a function of pulse period kept at a 2 % duty cycle. Films are intrinsic cadmium oxide grown on c-plane sapphire.
Figure A.20 Carrier concentration and mobility as a function of pulse period kept at a 6.4 % duty cycle. Films are intrinsic cadmium oxide grown on c-plane sapphire.
Figure A.21 Carrier concentration and mobility as a function of pulse period kept at a 12.0 % duty cycle. Films are intrinsic cadmium oxide grown on c-plane sapphire.