PULSED PECVD SYNTHESIS OF METAL DICHALCOGENIDE THIN FILMS

FOR SUSTAINABLE ENERGY APPLICATIONS

by

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A thesis submitted to the Faculty and Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science (Chemical Engineering).

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ABSTRACT

The current world energy demand is ~15 TW and growing, with >85% of production coming from non-renewable sources. The technologies for renewable energy exist, but to achieve this unprecedented scale of production at affordable cost will require developing alternative, earth abundant materials and develop new ways to produce them. Metal dichalcogenide (MS$_2$, MSe$_2$) are a class of semiconductors with unique optical, electrical and catalytic properties with potential applications in sustainability. The aim of this thesis was to develop a pulsed plasma-enhanced chemical vapor deposition (PECVD) as a novel approach for well controlled synthesis of stoichiometric thin films of FeS$_2$ and WS$_2$, establish their intrinsic material properties, and explore their potential in renewable energy applications.

First, pulsed PECVD was developed for self-limiting growth of pyrite (cubic FeS$_2$), a potential absorber for thin film solar cells. This material has promising attributes for photovoltaics, but poor device performance experienced to date has been attributed to the difficulty of controlling stoichiometry, avoiding marcasite phase impurities (orthorhombic FeS$_2$), and surface defects. To mitigate these issues, several techniques rely on a post deposition sulfur annealing step, which would not be amenable for large scale manufacturing. In this work, self-limiting growth of FeS$_2$ was accomplished using a continuous flow of Fe(CO)$_5$ and H$_2$S diluted in argon. The onset of thermal CVD was identified to be at ~300 °C, and films produced by thermal CVD contained sub-stoichiometric pyrrhotite. In contrast, pulsed PECVD produced stoichiometric FeS$_2$ films without the need for post-deposition sulfurization. Films contained a mixture of pyrite and marcasite, though the latter could be minimized using a combination of high duty cycle, low temperature, and low plasma power. Conversely, marcasite rich films could be produced using low duty cycles and high plasma power.
Both pyrite- and marcasite-rich films displayed similar optical properties with a band gap of ~1 eV and an absorption coefficient of ~$10^5$ cm$^{-1}$. Pyrite displayed relatively higher photoconductivity, but the absolute response was poor and solid-state devices fabricated with pyrite showed no rectifying behavior, indicating that this material may not be suitable for PV. Another energy application explored was the use of FeS$_2$ as a cathode for Li batteries because of its high energy density. Here the composition was shown to have an impact. Pyrite films showed high initial discharges near 890 mA*hr/g. Similar capacities were observed initially for marcasite, but these films degenerated after a few cycles.

The generality of pulsed PECVD for dichalcogenide synthesis was tested by applying the lessons gained from depositing pyrite to WS$_2$. Stoichiometric WS$_2$ thin films were produced by simply replacing Fe(CO)$_5$ with W(CO)$_6$. Films were deposited by thermal CVD and continuous wave (CW) PECVD for comparison, and it was found that pulsed PECVD delivered the best crystalline quality at combinations of high plasma power and intermediate duty cycles ($\tau = 0.50 - 0.67$). This was attributed to the observation that pulsing produced transients with significantly enhanced plasma intensity relative to CW PECVD. Moreover the orientation of the films could be controlled through choice of duty cycle and thickness. WS$_2$ was demonstrated to be catalytically active for hydrogen evolution reaction (HER), as films deposited on fluorine-doped tin oxide with an increased density of edge sites was shown to reduce the HER onset potential from 340 mV to 240 mV vs. RHE. Pulsed PECVD may also be promising for synthesizing WS$_2$ nanocrystals, which could be formed in abundance under certain operating conditions.
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CHAPTER 1
INTRODUCTION

Innovation in energy research will be vital for improving cost and enabling large scale
deployment of renewable energies to deliver the 10 - 20 TW of power needed to supply the
world energy demand by 2050 and stabilize CO₂ emissions [1, 2]. Solar energy is one of the
most promising areas because only a fraction of the 120,000 TW that the sun provides the earth
needs to be harnessed [2]. To meet the terawatt challenge, world solar production will needs to
increase 50 fold from ~ 20 GW/yr to > 1 TW/yr, and require production on the scale of ~5 x 10¹⁰
m²/yr [3]. While crystalline silicon represents the majority of the solar market, a new generation
of thin film cells is being developed to reduce material costs. The leading materials for thin film
photovoltaics, CdTe and CuInGaSe (CIGS), have both been deployed commercially and record
efficiencies are > 20%. However the materials are either toxic or their lack of earth abundance,
particularly Te and In, may limit capacity for meeting world energy demand [4]. This has
brought renewed interest into earth abundant materials.

Among potential candidates, pyrite (cubic FeS₂) has been proposed as the most promising
because of the abundance and ease of extraction of Fe and S [5]. It also has a suitable band gap,
~0.95 eV [6], and a strong absorption coefficient, ~10⁵ cm⁻¹ that enables 90% light to be
absorbed in 100 nm, compatible with its minority carrier diffusion length (100 - 1000 nm) [7].
Target efficiencies have been proposed at 18.5% [8], but actual device results have been largely
unsuccessful [9]. There have been a few proposed reasons for the poor performance. One
possibility is pyrite's optoelectronic properties is susceptible to impurities such as
substoichiometric FeS₂₋ₓ or marcasite (orthorhombic FeS₂) [10, 11]. Another possibility is that
surface states cause Fermi level pinning [7]. Research into new synthesis techniques has continued to better understand these issues.

An equally important engineering challenge for achieving the terawatt challenge is improving energy storage [2]. Part of the storage needs are driven directly by solar and wind, where energy production depends on daylight and weather and cannot provide a steady supply to match demand. Another need for storage is to provide energy for vehicles and mobile devices. Pyrite is of interest for energy storage as a cathode material for Li ion batteries because of its high specific energy (~1300 Wh/kg) [12]. While it has been successful as a primary battery, it has had poor rechargeability. Research has focused on improving its secondary use and evaluating it for advanced applications such as electric vehicles and microelectronic mechanical systems (MEMS) [13, 14].

Another potential avenue for energy storage is production of hydrogen to replace fossil fuels. The benefit for a renewable hydrogen economy is that H₂ has no CO₂ emissions when combusted, but the biggest challenge is finding a source [15]. Steam reforming of methane is the most widely used technique for making H₂, but this require fossil fuel and is not carbon neutral [16]. A sustainable approach is to use excess energy from solar and wind for water splitting [17]. Photo- or electrochemical water splitting entails both the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), driven by an electrical potential. Catalysts are used to reduce the kinetic energy barrier for the reaction and improve the efficiency of the process. The best catalyst for this is Pt, which requires a negligible over-potential [18]. However, Pt is expensive, not abundant and not practical to fully realize the hydrogen economy. Assuming conversion of all trucks and cars to fuel cells, estimates for 2040 for U.S. H₂ production would require 150 megatons per year, compared to ~ 10 megatons per year produced
Research has focused to find earth abundant alternatives to Pt. Promising materials have included MoS\textsubscript{2} and WS\textsubscript{2}. While many studies have focused MoS\textsubscript{2}, more research on WS\textsubscript{2} is required to understand its full potential for applications such as electrocatalyst.

In this thesis, FeS\textsubscript{2} and WS\textsubscript{2} thin films were deposited by a new method, pulsed plasma enhanced chemical vapor deposition (PECVD). This technique enables digital control of film growth to \(~1\text{ Å/pulse}\) at faster rates than atomic layer deposition (ALD) and requires lower thermal budget than conventional thermal CVD, which would be advantageous for large scale manufacturing. In this work, operating parameters including duty cycle (\(\tau\)), power, substrate temperature (\(T_s\)), pressure, and precursor flow rates were explored to determine the effect on growth rate and film quality. The specific goals for the thesis was to first, establish the parameter space for self-limiting deposition of stoichiometric, phase pure pyrite by pulsed without the need for post-deposition sulfurization. Second, the goal was to characterize the optoelectronic properties of FeS\textsubscript{2} films as a solar absorber, evaluate performance as a cathode for Li-ion batteries, and determine if these properties were phase dependent. The third goal was to explore the parameter space for pulsed-PECVD for the deposition of another dichalcogenide, WS\textsubscript{2}, and demonstrate the application of these films as an electrocatalyst for the HER.
CHAPTER 2
EXPERIMENTAL

This chapter provides an in-depth description of pulsed PECVD and details of the experimental setup. Also included is a description of the primary characterization techniques used in this thesis including Raman spectroscopy, X-ray diffraction, UV-VIS-NIR spectrophotometry, FE-SEM, EDAX, conductivity experiments, I-V characterization, and electrochemical cells.

2.1 Principles of Pulsed PECVD

Pulsed PECVD is a 2-step process, represented in Figure 2.1. During pulsed PECVD, there is continuous delivery of the metal precursor and \( \text{H}_2\text{S} \), both diluted in argon. The plasma is then pulsed on and off using a square wave modulation at low frequency, 0.1 - 1 Hz.

![Figure 2.1: Basic steps of Pulsed PECVD](image)

For pulsed PECVD to be self-limiting, there are two conditions that must be met:

1. There is no thermal CVD, no growth during the plasma off step
2. There is no deposition under CW operation, where precursor is fully reacted and sacrificially deposited

When these two conditions are met, the film growth can be digitally controlled at \(~1 \, \text{Å/pulse}\) levels. Figure 2.2 describes the two mechanisms that can contribute to growth during pulsed
PECVD. Mode I is "ALD like" where the precursor can adsorb to the surface during the plasma off step. At plasma ignition, an abundance of atomic S is generated that will sulfurize the precursor to produce the film. The second type, Mode II, is "PECVD like". The partial pressure of the precursor will increase during the plasma off step, and at plasma ignition it will dissociate to produce reactive intermediate species that can be deposited.

Figure 2.2: Deposition mechanism of pulsed PECVD

Deposition of FeS$_2$ was found to meet both criteria 1 and 2 at temperatures <280 °C. The lowest rf power that produced a stable plasma was 15 W, and even at this condition the IPC decomposed in the plasma and was sacrificially deposited without reaching the substrate. IPC readily decomposes in the presence of a plasma, as evidenced by pulsed PECVD experiments with only a mixture of IPC and Ar and no H$_2$S resulted in the deposition of iron powder. The deposition rate was controlled by the availability of IPC as indicated by the strong correlation between GPC and plasma off time, which suggests that growth proceeds predominately through
mode II. Deposition of FeS$_2$ was only achievable by pulsed PECVD under the conditions explored, because this enables appreciable concentration of IPC to build in close proximity to the substrate during the plasma off step so that they can contribute to deposition at plasma ignition.

2.2 Pulsed-PECVD Setup

Figure 2.3 shows a schematic diagram of the pulsed PECVD reactor and Table 2.1 provides the list of components involved. The deposition chamber consisted of capacitive-coupled parallel plate reactor. Plasma was generated by 13.56 MHz RF source and a custom matching network was used to minimize reflected power. Flow of precursors was controlled

![Schematic diagram of pulsed PECVD reactor](image-url)
with a bubbler, which used Ar controlled by a mass flow controller (MFC) as the carrier gas. The H$_2$S was diluted to 10% in Ar and also controlled by an MFC. The reactor was evacuated with a mechanical vacuum pump and a third MFC was used to add additional Ar to control pressure. Prior to starting WS$_2$ experiments, the vacuum pump was switch for a higher capacity model, noted in Table 2.1. All gases were mixed and delivered to the chamber through a 13.9 cm diameter showerhead that also served as the powered electrode. The substrates were attached to the grounded electrode located 5.7 cm above the showerhead and held in place with a combination of metal holders and Kapton tape. Substrates were heated with a resistance heater that was controlled with a variac and temperature was monitored with a thermocouple. Pulsing frequency and plasma power was controlled with Labview. The plasma was characterized using an optical emission spectrometer (OES) positioned outside a site glass.

Table 2.1: Summary of equipment used for the pulsed PECVD reactor

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$S/Ar MFC</td>
<td>Unit Instruments, UFC 1020 (420 sccm max)</td>
</tr>
<tr>
<td>Bubbler MFC</td>
<td>Unit Instruments, UFC 1400 (70 sccm max)</td>
</tr>
<tr>
<td>Ar MFC</td>
<td>Unit Instruments, UFC 1200 (695 sccm max)</td>
</tr>
<tr>
<td>RF generator</td>
<td>Advanced Energy RFX 600A</td>
</tr>
<tr>
<td>OES</td>
<td>Ocean Optics SD2000, software: OOIBase 32</td>
</tr>
<tr>
<td>Vacuum pump (FeS$_2$ work)</td>
<td>Edwards E2M30</td>
</tr>
<tr>
<td>Vacuum pump (WS$_2$ work)</td>
<td>Edwards E2M80</td>
</tr>
<tr>
<td>Reactor Pressure Indicator</td>
<td>MKS Baratron 127 Pressure Transducer, 10 Torr max</td>
</tr>
<tr>
<td>Bubbler Pressure Indicator</td>
<td>MKS Baratron 122B Pressure Transducer, 1000 Torr max</td>
</tr>
<tr>
<td>IPC Chiller</td>
<td>NesLab RTE-111</td>
</tr>
<tr>
<td>W(CO)$_6$ Heater</td>
<td>NesLab RTE-100</td>
</tr>
</tbody>
</table>

2.3 Metal Precursor Bubbler

A basic schematic of the bubbler is also shown in Figure 2.3. Precursors (Fe(CO)$_5$, W(CO)$_6$) were stored in a vessel that was submersed in a heater/chiller bath that was temperature controlled. The Ar carrier was introduced at the bottom of the vessel, and the precursor/Ar
mixture exited at the top. The bubbler pressure ($P_{\text{bubbler}}$) was measured with a capacitive manometer and controlled manually with a needle valve placed downstream. Equation 2.1 was used to calculate precursor flow rate, and Equation 2.2 and 2.3 are the Antoine's equations used to calculate vapor pressure ($P^*$) for Fe(CO)$_5$ and W(CO)$_6$, respectively.

$$F_{\text{precursor}} = \frac{F_{Ar}P^*}{P_{\text{bubbler}}}$$  \hspace{1cm} (2.1)

$$\log(P^*_{\text{Fe(CO)}_5}(kPa)) = 3.90 - \frac{1258}{T(K)} - 61.6$$  \hspace{1cm} (2.2)

$$\log(P^*_{\text{W(CO)}_6}(\text{bar})) = 11.096 - \frac{4060}{T(K)}$$  \hspace{1cm} (2.3)

### 2.4 Raman Spectroscopy

Raman spectroscopy was used to characterize the molecular bonding in the films. This technique uses a laser to excite material and measure Raman scattering of low-frequency vibrational modes. The instrument was a WITech Alpha 300R Confocal Raman Microscope at an excitation wavelength of 532 nm and 100X magnification. Oscilloscope mode was used to adjust the laser intensity to achieve sufficient signal to noise. Films analyzed were deposited on Si, and spectra shifted to center the Si peak at 520 cm$^{-1}$. Spectra are an average of 3 scans, each lasting 30 seconds for FeS$_2$ and 10 seconds for WS$_2$. Settings used were the following: T1 grating, 1800 g/min, BLZ 500 nm, and center wavelength 550 nm. Patterns were normalized to maximum signal intensity for comparison purposes.

### 2.5 XRD

X-ray diffraction (XRD) was used to characterize the crystal phases for deposited films. The technique involves the detection of angles of constructive diffraction of X-rays from crystalline
patterns, based upon Bragg's law, equation 2.4 and Figure 2.4. All diffraction patterns were matched to FeS$_2$ and WS$_2$ reference patterns, summarized in Table 2.2. Scans were performed on films deposited on silicon substrates with a Siemens D500 diffractometer using Cu K$_\alpha$ ($\lambda = 1.54$ Å) X-ray source. Samples were given a slight tilt to avoid interference from the silicon substrate. FeS$_2$ samples were scanned using 0.05° steps and 5 sec count time. WS$_2$ samples were scanned at 0.05° steps and 3 sec count time. Patterns were normalized to maximum signal intensity for comparison purposes.

$$2d \sin \theta = n\lambda$$

(2.4)

![Figure 2.4: Principle and key variables for Bragg's Law](image)

Table 2.2: Summary of XRD reference patterns used to identify crystal phases

<table>
<thead>
<tr>
<th>Crystal Phase</th>
<th>Reference Pattern</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrite</td>
<td>71-2219</td>
</tr>
<tr>
<td>Marcasite</td>
<td>74-1015</td>
</tr>
<tr>
<td>Pyrrhotite</td>
<td>74-1051</td>
</tr>
<tr>
<td>Tungsten Sulfide</td>
<td>84-1399</td>
</tr>
</tbody>
</table>
2.6 FE-SEM

Field emission scanning electron microscope (FE-SEM), model JEOL JSM-7000F, was used to image the top of films and to measure cross-section thickness. Cross sections were achieved by scoring and splitting films deposited on Si wafers. Imaging was performed using 5 kV accelerating voltage, low current, and working distances of 4 and 6 mm.

2.7 EDAX

An energy dispersive X-ray analysis (EDAX) unit attached to the FESEM was used to determine the atomic ratios of S:Fe and S:W. The basis of this technique is that the accelerated electrons will collide with atoms and excite core electrons that will then emit X-rays with a characteristic energy (Figure 2.5). EDAX was measured using a 5 kV accelerating voltage, 10 mm working distance, 35° take-off angle, 25X magnification, and was calibrated to FeS$_2$ and WS$_2$ standards (Ted Pella) using the EDAX Genesis software. Reported values were averaged from three different locations on each film. Results for FeS$_2$ were found to be thickness dependent for films < 200 nm. The primary cause is that the characteristic X-ray for Fe, 0.7 keV, is lower in energy than for S, 2.3 keV. Sampling of Fe can occur at greater depths than S, because it requires less energy retained by the electron probe to generate an X-ray. When a thin film is calibrated to bulk FeS$_2$, it will appear to have less iron and S:Fe will be > 2:1. One way to reduce this error was to use lower accelerating voltages (5 kV instead of 10 kV), which will reduce the sampling depth. The remaining error was corrected using the Pouchou and Pichoir model for stratified specimens [19], which considers additional factors such as atomic mass and size and the samples mass density at different depths. Thickness was not an issue for WS$_2$, mostly due to higher energy of the characteristic X-ray of W (1.8 keV).
Figure 2.5: Monte Carlo simulation of the emission of Fe-L X-ray (0.7 keV) in bulk FeS$_2$ from a 5 kV electron beam. Intensity is indicated by shades of red, with white representing the maximum intensity. Simulation was generated with NIST DSTA-II.

2.8 UV-VIS-NIR Spectrophotometry

Transmittance and reflectance was measured for films deposited on FTO using a Cary 5G UV-Vis-NIR spectrophotometer with an integrating sphere, which was corrected for background. Absorbance was calculated by subtracting transmittance and reflectance from 100%. Absorption coefficients, $\alpha$, were calculated using Beer's law, equation 2.5:

$$T = 10^{-\alpha \ell}$$  \hspace{1cm} (2.5)

Both FeS$_2$ and WS$_2$ films displayed a high level of specular reflectance that was independent of film thickness, and so transmittance was normalized to exclude reflected light when calculating absorption coefficients.
2.9 HER testing

Polarization curves were measured using Gamry PCI4 Potentiostat at a scan rate of 5 mV/s. Figure 2.6 is a basic diagram of the experimental setup. Films deposited on FTO functioned as the working electrode and a Pt mesh was used as a counter electrode. The electrolyte was 0.5 M H₂SO₄ and a Ag/AgCl electrode served as a voltage reference. Sample area was measure and used to determine current density.

![Experimental diagram of HER testing](image)

Figure 2.6: Experimental diagram of HER testing

Voltage was correct for pH and reported versus the reversible hydrogen electrode (RHE) using equation 2.6. The onset potential was first determined by fitting current density data between 0 and -0.05 V vs RHE to a linear plot, as shown in Figure 2.7. The voltage at which measured current density was greater than 0.5 mA/cm² from the linear plot was used to determine onset potential.

\[ E(RHE) = E(Ag/AgCl) + 0.197V + 0.0591 \cdot pH \]  

(2.6)
2.10 Conductivity Experiments

Sheet resistance was measured on films deposited on non-conductive glass using a 4-point probe. The measure value was multiplied by film thickness to get resistivity and conductivity. Photoconductivity was also measured with the 4-point probe, where films were first illuminated for 3 minutes with a Cole-Parmer Instrument Fiber Optic Illuminator, Model 41500-50, set to maximum intensity and positioned ~2 cm from the film.

2.11 I-V characterization

Figure 2.7 shows the device structures tested. Schottky diodes were produced first by depositing FeS₂ films onto FTO coated glass and completed by evaporation of metal (Au, Cu, Al) dots with ~75 nm thickness and 11 mm diameter. A fourth device structure was produced
by depositing FeS$_2$ onto 100 nm CdS on FTO. Evaporated gold dots were used for back contacts onto FeS$_2$.

![Diagram of device scheme used for I-V characterization](image)

**Figure 2.8: Diagram of device scheme used for I-V characterization**

### 2.12 FeS$_2$ Battery Testing

For battery testing, ~300 nm films were deposited onto FTO. The electrochemical performance was determined by performing cyclic voltammetry (CV) at a 0.1 mV/s scan rate and discharge-charge at constant current using a BioLogic VMP3 multichannel potentiostat. The exposed sample area was 1 cm$^2$. All samples were examined using a two-electrode geometry with Li metal serving as both the counter and reference electrode. The electrolyte was 1 M Li perchlorate dissolved in propylene carbonate, and all testing was conducted in an inert atmosphere.
CHAPTER 3

SELF LIMITING DEPOSITION OF PYRITE ABSORBERS BY PULSED PECVD

This is a paper that was published in the Journal of Vacuum Science and Technology - A in November 2013. It has been reformatted for this thesis.

Christopher D. Sentman¹,², Maria O’Brien³ and Colin A. Wolden¹,⁴

Self-limiting growth of pyrite thin films was accomplished by pulsed plasma-enhanced chemical vapor deposition (PECVD) with continuous delivery of iron pentacarbonyl diluted in a mixture of H₂S and argon. The growth rate per cycle was controlled between 0.1 – 1 Å/pulse by adjusting the duty cycle and/or plasma power. The onset of thermal CVD was identified at ~300 °C, and this process resulted in films containing sub-stoichiometric pyrrhotite. In contrast, pulsed PECVD produced stoichiometric FeS₂ films without the need for post-deposition sulfurization. Films contained a mixture of pyrite and marcasite, though the latter could be attenuated using a combination of high duty cycle, low temperature, and low plasma power. Pulsed PECVD films displayed similar optical properties with a band gap of ~1 eV and an absorption coefficient of ~10⁵ cm⁻¹, regardless of the pyrite:marcasite ratio.

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3.1 Introduction

Pyrite, FeS$_2$, is a non-toxic, earth abundant semiconductor that offers promise for sustainable energy applications. Its high theoretical specific energy capacity (~1300 Wh/kg) makes it an attractive material to serve as the cathode in Li ion batteries, offering superior performance and longevity relative to alkaline cells [12]. Thin film Li/FeS$_2$ cells with a polymer electrolyte are a promising candidate for rechargeable batteries for electric vehicles or as microbatteries in micro-electronic mechanical systems (MEMS) [13, 14]. The potential of pyrite for solar energy conversion was first recognized in the 1980s and developed by Tributsch and co-workers [7]. It has received renewed attention due to its earth abundance and ease of extraction [5]. It has a large absorption coefficient (> $10^5$ cm$^{-1}$) that enables >90% of light to be captured within a 100 nm film, which is compatible with its minority carrier diffusion length (100 – 1000 nm) [7]. Its optical band gap of ~0.95 eV is quite suitable for the harnessing of solar energy [6]. The best results to date have been achieved in photoelectrochemical cells that have shown large photocurrent (up to 42 mA/cm$^2$), but suffer from low $V_{oc}$ (< 200 mV) and poor efficiencies (< 3%) [7]. Attempts to incorporate pyrite in solid state devices have been largely unsuccessful [9]. The exact causes of the low $V_{oc}$ are not fully understood. The presence of impurities such as marcasite (orthorhombic FeS$_2$) or sub-stoichiometric compounds is one possibility [10, 11]. Other concerns include sulfur vacancies, particularly at the pyrite surface, which may reconstruct and lead to Fermi level pinning [7, 20]. This has motivated further research into developing new synthesis techniques to both better understand and resolve these issues.

Techniques used to deposit pyrite thin films have included physical vapor deposition (PVD), chemical vapor deposition (CVD), and solution-based processes. PVD methods have
typically involved magnetron sputtering of iron-containing targets, either in a reactive H2S/Ar ambient [21] or in conjunction with subsequent annealing in a sulfur-containing atmosphere [22, 23]. Pyrite CVD has been performed at both atmospheric and reduced pressures, forming pyrite through the reaction of gaseous iron and sulfur precursors on a substrate at elevated temperatures [24-27]. One solution chemistry approach relies on first synthesizing pyrite nanocrystals [28, 29], which are subsequently suspended to form an ink and deposited as a thin film through techniques such as dip or spin coating [9, 20, 30]. Solutions methods also include the deposition of Fe2O3 films through sol-gel or chemical bath deposition, followed by sulfurization to convert to pyrite [31, 32].

Some methods such as reactive sputtering [21] or thermal CVD [24, 25, 27] have produced FeS2 directly. However many other techniques first produce Fe or Fe2O3, which are subsequently converted to pyrite through a post-deposition annealing step in a sulfur atmosphere. Moreover, sulfur deficient films produced by sputtering [23] or CVD [26] have also been shown to benefit from post-deposition sulfurization. This step is typically conducted by sealing the sample and a precise amount of sulfur into a quartz ampoule under inert conditions followed by heating to temperatures of 400 - 700 °C for durations of 1 - 8 hrs [22, 23, 28, 30, 31, 33]. For best results it is also imperative to position the substrates within the annealing chamber in such a way to prevent the condensation of excess sulfur on the sample during cooling. The amount of sulfur is used to control the partial pressure, while the elevated temperature promotes sulfur diffusion and provides the driving force to form the thermodynamically favored pyrite phase. The specific conditions employed can influence the ratio of pyrite to marcasite in the resulting films [26, 30, 33]. In addition to its cumbersome nature, Zhang et al. [33] have shown that
sulfurization of iron films is diffusion-limited, and that without proper care nanoscale impurities may persist in the material that are undetectable using common characterization techniques.

Due to its extraordinarily high absorption coefficient, ultrathin pyrite films could be potentially useful either directly or as a sensitizing agent [34, 35]. As such it would be desirable to develop techniques to deposit pyrite thin films with atomic level control over thickness. Atomic layer deposition (ALD) would be a natural approach, but to date precursors are not available with the appropriate surface chemistry to deliver self-limiting behavior. In this work we describe the use of pulsed plasma-enhanced chemical vapor deposition (PECVD) for self-limiting growth (i.e. 1 Å/pulse) of pyrite. This process is performed at low temperature relative to conventional techniques, which expands the range of substrate materials that could be employed for device fabrication. In addition, an objective of this work was to deposit pyrite in one step without the need for post-deposition sulfur annealing, which would be critical for large-scale commercialization of this material.

3.2 Principles of pulsed PECVD

Our group has previously established pulsed PECVD as an alternative to ALD for self-limiting growth of several metal oxide films [36-39]. ALD is a four-step process where two reactants are sequentially exposed to the substrate but separated by purge steps to prevent direct reaction between the two precursors. In contrast, pulsed PECVD delivers both reagents continuously and discrete growth is achieved by pulsing the plasma on and off using square wave modulation at low frequency (~1 Hz). Pulsed PECVD offers process simplifications with respect to gas handling, and the elimination of purge steps reduces cycle times and enhances net deposition rates. There are two conditions that must be met to ensure that pulsed PECVD
provides the digital control of a self-limiting growth technique. First, the reagents must be thermally inert so that there is no CVD in the absence of plasma. Second, there is no deposition under continuous wave (CW) plasma operation. This second constraint is typically achieved by diluting the metal precursor such that it is completely consumed either in the plasma or sacrificially deposited before reaching the substrate [37]. While no growth is observed with the plasma continuously on or with it off, discrete growth is readily observed when the plasma is pulsed at low frequency.

There are two potential contributors to growth during pulsed PECVD [37]. The first mode is an ALD-like contribution due to adsorption of the metal precursor during the plasma off-time, followed by subsequent conversion during the plasma exposure step. The second contribution is a CVD-like growth component attributed to reactive species produced near the substrate at plasma ignition. Through this second mode pulsed PECVD can be used to deliver self-limiting growth from precursors that are not suitable for ALD, for example the formation of SiO₂ from SiCl₄ [39]. By controlling variables such as partial pressure and plasma duty cycle the amount of growth per cycle (GPC) can be modulated over a broad range (0.1 – 5 Å/pulse).

Precursor selection is important for developing a successful pulsed PECVD process, and the CVD literature on pyrite provides useful guidelines. For pulsed PECVD the metal precursor should be thermally inert, but readily releases its ligands upon plasma exposure. Vapor-phase precursor options for iron are fairly limited, with most CVD investigations focused on either iron acetylacetonate (Fe(acac)₃) [26, 27] or iron pentacarbonyl (IPC, Fe(CO)₅) [24, 25]. Fe(acac)₃ has been selected over IPC since the latter begins to decompose into iron powder at temperatures as low as 150 °C, well below the requirement to thermally convert iron into pyrite. Those who have employed IPC for thermal CVD have taken special care in reactor design/operation to
prevent premature decomposition prior to reaching the substrate [24, 25]. A drawback of Fe(acac)$_3$ is that the ligand has limited volatility, leading to the potential of significant carbon contamination during plasma exposure. A demonstrated benefit of pulsed PECVD is that high quality material can be deposited at significantly lower temperature than in CVD, due to the chemical energy provided by the plasma. As such we chose IPC since low temperature operation mitigates decomposition concerns, and the volatility of the CO ligands should enhance both conversion and film purity. IPC also has a high vapor pressure (P* ~3.7 kPa at 25 °C) that simplifies vapor delivery and control.

With respect to the sulfur precursors the predominant choices in pyrite CVD have been tert-butyl disulfide (TBDS, (CH$_3$)$_3$-C-S-S-C-(CH$_3$)$_3$) [25-27] and hydrogen sulfide (H$_2$S) [24, 25]. The sulfur precursor has most frequently been TBDS because it is thermally more reactive with iron than H$_2$S. However, non-equilibrium plasmas have been shown to readily decompose H$_2$S into its atomic constituents [40], and the chemical potential of atomic sulfur is ~3 eV greater than H$_2$S. Recently we demonstrated the efficacy of plasma-activated H$_2$S for the conversion of hematite nanorods into stoichiometric FeS$_2$ [32]. Another advantage of H$_2$S is that the hydrogen released by plasma dissociation readily leaves the chamber, whereas the ligands associated with TBDS would be expected to result in extensive carbon deposition. During the plasma on step the sample exposure to atomic sulfur serves as an *in situ* annealing procedure, and since the amount of growth per cycle is just ~1 Å/pulse, diffusion limitations are not expected to be a concern.

In this study we demonstrate and establish the parameter space for self-limiting deposition of pyrite by pulsed PECVD. Stoichiometric FeS$_2$ films are produced at low temperature without the need for post-deposition sulfurization. Furthermore we describe the
sensitivity of growth rate and quality to process parameters by quantifying the structure, morphology, and optical properties of the resulting films.

3.3 Experiment - Film Deposition

Pulsed PECVD was performed in a capacitively coupled parallel plate reactor evacuated by a mechanical pump to a base pressure < 1 Pa. Reactants were premixed and delivered through a 13.9 cm diameter showerhead, which also served as the powered electrode. A matching network ensured that the reflected power was negligible. A mixture of 10% H₂S in argon (Air Liquide) was controlled by a mass flow controller (MFC) at flowrates between 40 – 120 sccm. Iron pentacarbonyl (99.5%, Strem Chemicals) was stored in a bubbler at 5 °C and 66 kPa and argon controlled by an MFC was used as the carrier gas [41]. A third MFC was used to add variable amounts of argon (20 – 110 sccm) to ensure all experiments were performed at a pressure of 53 Pa. Substrates included both silicon (100) wafers and fluorine doped tin oxide (FTO) coated glass (TEC 15, Hartford Glass) with a nominal size of 3.5 cm × 3.5 cm. FTO coated glass was sonicated in a solution of Alconox cleaning detergent for 5 minutes and then rinsed consecutively with DI water, acetone, and methanol. Silicon substrates were dipped in a 2% HF solution to remove native oxide. Substrates were attached to the center of the grounded electrode located 5.7 cm above the showerhead. Substrates were heated with a resistance heater and the temperature was monitored with a thermocouple. An optical emission spectrometer (OES) was positioned outside the reactor to monitor the emission spectrum of the plasma through a site glass. Further details on the experimental setup is provided elsewhere [42].

Preliminary experiments were performed to identify the critical variables and establish the parameter space for this work. Table 3.1 summarizes the baseline values for these
parameters and the ranges explored. In this work the IPC bubbler conditions were fixed to deliver IPC at a constant flowrate of 0.25 sccm. H₂S was supplied in excess to ensure full conversion to stoichiometric FeS₂. H₂S:IPC ratios in the range of 16 - 48 were explored and found to have a negligible impact on deposition rate, film composition, or optical properties. For films produced in this work the ratio was fixed at H₂S:IPC = 36. The sensitivity of the process to pressure was explored over a range of 53 - 93 Pa. This variable also had no impact on the deposition process, and the pressure was fixed at 53 Pa. Below we report on the variables that were found to most strongly impact deposition rate and quality: duty cycle (τ), substrate temperature (Tₛ), and plasma power.

Table 3.1: Summary of the baseline conditions and the process space discussed in this work.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Baseline</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plasma off time, t_{off} (s)</td>
<td>1</td>
<td>0.5 – 5</td>
</tr>
<tr>
<td>Plasma on time, t_{on} (s)</td>
<td>2</td>
<td>1 – 6</td>
</tr>
<tr>
<td>Duty Cycle (τ)</td>
<td>0.67</td>
<td>0.17 – 0.86</td>
</tr>
<tr>
<td>Substrate Temperature (ºC)</td>
<td>240</td>
<td>180 – 380</td>
</tr>
<tr>
<td>RF Power (W)</td>
<td>50</td>
<td>15 – 100</td>
</tr>
<tr>
<td>IPC Flowrate (sccm)</td>
<td>0.25</td>
<td>Fixed</td>
</tr>
<tr>
<td>H₂S:IPC Ratio</td>
<td>36</td>
<td>Fixed</td>
</tr>
<tr>
<td>Pressure (Pa)</td>
<td>53</td>
<td>Fixed</td>
</tr>
</tbody>
</table>

3.4 Experiment - Film Characterization

Film thickness and deposition rate were quantified by imaging cross-sections of samples deposited on silicon with a JEOL JSM-7000F field emission scanning electron microscope (FE-SEM). An EDAX electron dispersive x-ray spectrometer (EDS) attached to the FE-SEM was used to determine film stoichiometry. EDS was measured using at 5 kV accelerating voltage and calibrated based on a pyrite standard (Ted Pella). However for thin films (< 200 nm) we
observed that this procedure yielded S:Fe ratios much greater than 2:1, a problem that was exacerbated as the thickness was reduced. This source of error was previously reported by Ares et al. [43]. To correct for film thickness, EDAX measurements were quantified using the PAP $\phi(\rho z)$ model developed by Pichoir and Pouchou for stratified specimens [19]. EDAX measurements were the most reproducible for film thicknesses $\geq 100$ nm, and we limit our reporting of composition to these samples. X-ray diffraction (XRD) was measured with a Siemens D500 diffractometer with a Cu K$\alpha$ ($\lambda = 1.54$ Å) X-ray source. Raman spectra were collected with a WITec Alpha 300R Confocal Raman Microscope at an excitation wavelength of $\lambda = 532$ nm and 100X magnification. Optical properties were measured with a Cary 5G UV-Vis-NIR spectrophotometer equipped with an integrating sphere. Transmittance and reflectance were measured between $\lambda = 1500 – 350$ nm, and the contributions of the underlying FTO-coated glass were background subtracted.

3.5 Results and Discussion

We first present the impact of duty cycle on the growth per cycle and composition by independently varying both the plasma on and off time. Next, the role of substrate temperature was explored. The threshold for thermal CVD is identified and its ramifications for film properties are described. The influence of RF power on both plasma characteristics and deposition are discussed. Note that these studies often produced films with varying total thickness. However, additional studies were performed at fixed conditions with the total number of cycles varied to produce films with thicknesses between 30-300 nm. These experiments showed that the trends in composition/quality discussed below are independent of film thickness.
We conclude with a discussion of the optical properties of films deposited under various conditions.

3.5.1 Self-limiting Deposition and Duty Cycle

The self-limiting nature of the pulsed PECVD process was confirmed by first observing that no thermal CVD occurs with a continuous delivery of both reactants at $T_s = 240 \, ^\circ C$ in the absence of plasma. Likewise, no deposition was observed during CW plasma operation over the power range explored (15 – 100 W). Images of the FTO glass substrates from these experiments are provided in Figure 1a. Under the same reactor conditions, pulsing the plasma at a duty cycle of $\tau = 0.5$ produced the strongly absorbing iron disulfide film pictured in Fig. 3.1a.

![Figure 3.1: (a) Photographs of glass substrates after 15 minutes of exposure to reactants at $T_s = 240 \, ^\circ C$ with no plasma, pulsed plasma, and continuous plasma; (b) Growth per cycle as a function of duty cycle ($\tau$) at fixed on time and off time of 1 second; (c) film stoichiometry as a function of duty cycle.](image)
The importance of duty cycle on rate and quality was examined by fixing either the $t_{on}$ or $t_{off}$ at 1 sec, and varying the other parameter. The substrate temperature and RF power were fixed at 240 °C and 50 W, respectively. Figure 3.1b shows the relationship of deposition rate with duty cycle. With $t_{on} = 1$ sec, the growth per cycle increased from 0.1 to 1.0 Å/pulse as duty cycle was reduced from 0.67 to 0.17. In contrast, with $t_{off}$ fixed at 1 sec the GPC was essentially independent of duty cycle at a value of 0.34 Å/pulse. The insensitivity of GPC to plasma on time suggests that plasma consumption of IPC is very fast ($<< 1$ s) and that the plasma exposure step is primarily for removing ligands and producing stoichiometric films. The GPC value was controlled by the plasma off time, and the dependence was consistent with the residence time of the reactor. Based on the volumetric flowrate and estimates of the chamber volume, the residence time was ~2 sec. At plasma extinction the density of IPC in the reactor is negligible. By approximating the low pressure reactor as a well mixed reactor, the time required for IPC concentration to reach steady state level is estimated to be 5 – 10 sec. The IPC concentration in the reactor at plasma ignition controls the amount of precursor available for deposition.

Figure 3.1c shows the stoichiometry as duty cycle was varied for films. As mentioned above, reporting is limited to films with a thickness $\geq 100$ nm. Within the accuracy of our techniques all pulsed PECVD films displayed the stoichiometric 2:1 sulfur to iron ratio, independent of process conditions. Note that neither C nor O were detected beyond background levels that were observed in all samples including the pyrite calibration standard, though if C and O impurities exist below the detection limit of our technique it may still affect optoelectronic properties. The crystal phases present were evaluated by XRD and Raman spectroscopy with selected results shown in Figure 3.2. The duty cycle was varied from $\tau = 0.20$ ($t_{off} = 4$ s, $t_{on} = 1$ s) to $\tau = 0.86$ ($t_{off} = 1$ s, $t_{on} = 6$ s). The XRD patterns show a mixture of pyrite and marcasite, but no sub-
stoichiometric compounds were detected. While pyrite and marcasite have several overlapping peaks, pyrite can be distinguished by its reflections at 28.5° (111), 40.7° (211), and 56.3° (311). Likewise, unique marcasite reflections appear at 25.9° (110), 39.0° (120), and 52.0° (211). Comparison of these peaks at different duty cycles shows that the pyrite fraction is enhanced with increasing duty cycle. This trend is confirmed by the Raman spectra shown in Figure 3.2b. The dominant bands observed are the $E_g$ and $A_g$ modes for pyrite at 343 cm$^{-1}$ and 377 cm$^{-1}$, respectively, and the $A_g$ mode for marcasite at 326 cm$^{-1}$ [44, 45]. The marcasite bands decrease relative to pyrite bands as duty cycle was increased from 0.20 to 0.67. However further increasing the duty cycle beyond $\tau = 0.67$ did not appreciably change the pyrite:marcasite ratio.

In addition, we examined the impact of post-deposition sulfurization by exposing films to an H$_2$S plasma for an hour at $T = 400$ °C. This treatment reduced the marcasite content for films that had a large marcasite fraction in the as-deposited state, but it had no detectable impact on films that originally contained a low marcasite fraction.

![Figure 3.2: Comparison of (a) XRD patterns and (b) Raman spectra as a function of duty cycle ($\tau$) from films deposited at $T_s = 240$ °C and 50 W identifying contributions from the pyrite (P) and marcasite (M) phases.](image-url)
3.5.2 Substrate Temperature

The substrate temperature was varied between $T_s = 40 - 380 \, ^\circ C$ with the plasma power and duty cycle held constant at 50 W and $\tau = 0.67$, respectively. At the lowest temperature of $T_s = 40 \, ^\circ C$ the substrate was covered by crystallized sulfur. This was not unexpected as the sulfur vapor pressure at this temperature is < 0.1 Pa, but this experiment confirmed that the plasma was effective for dissociating H$_2$S. Figure 3.3a displays growth per cycle as a function of temperature for $T_s = 180 - 380 \, ^\circ C$, conditions where no sulfur condensation was observed. Below 280 °C, the GPC is constant at ~0.3 Å/pulse, but above this point the growth per cycle increases linearly with substrate temperature. This increase is attributed to the onset of thermal CVD contributions to growth. This was verified by thermal CVD experiments as a function of temperature. Figure 3.3b displays photographs of substrates after exposure to reactants at selected substrate temperatures. These indicate that the critical temperature for the onset of thermal CVD occurs at $T_c \sim 300 \, ^\circ C$, at which point a faint film was observed after exposure to

![Figure 3.3: (a) Growth per cycle as a function of substrate temperature for films deposited at $\tau = 0.67$ and 50 W. (b) Photographs of substrates following thermal CVD experiments at selected temperatures.](image)
the reactants for 15 minutes. The onset of thermal CVD was in good agreement with pulsed PECVD data. At 350 °C and greater, a very distinguishable and thick film was formed. The onset of thermal CVD observed in this work is greater than the 150 °C reported in previous studies using IPC and H₂S [24, 25]. This might be explained by the differences in reactor pressure as previous studies were performed at atmospheric pressure [24] or 660 Pa [25], which is ~12 times greater the pressure used in our experiments.

The impact of thermal CVD contributions to the morphology and stoichiometry of the films as a function of temperature were evaluated by FESEM and EDAX. Figure 3.4 compares representative FESEM images of the morphology obtained from the three deposition regimes: (i) thermal CVD; (ii) pulsed PECVD at $T > T_c$; and (iii) pulsed PECVD at $T < T_c$. Films produced by thermal CVD film were very smooth with a homogenous, nanocrystalline grain structure (Fig. 3.4a). In contrast films produced at the same temperature by pulsed PECVD had a significantly different morphology (Fig. 3.4b). These films were significantly rougher, with larger, randomly oriented crystal grains are clearly visible. Figure 4c show a pulsed PECVD film at 240 °C, $T_s \leq T_c$, which displays a columnar grain structure and was quite smooth compared to the pulsed PECVD film at 380 °C. Within a deposition regime the morphology variations were not significant. The differences between thermal CVD and pulsed PECVD films were also manifested in film composition as shown in Figure 3.4d. The composition of all pulsed PECVD films, regardless if $T_s$ was greater or less than $T_c$, were stoichiometric within measurement error. In contrast, all thermal CVD films displayed sub-stoichiometric compositions with S:Fe ratios ranging from 1.5 – 1.7.

The differences in composition between thermal CVD and pulsed PECVD films were further corroborated by the XRD patterns shown in Figure 3.5a. Only weak reflections of pyrite
Figure 3.4: SEM cross-section images of films produced by (a) thermal CVD at 380 °C; (b) pulsed PECVD at 380 °C; (c) pulsed PECVD at 240 °C; and (d) film stoichiometry as a function of substrate temperature for pulsed PECVD and thermal CVD films.

and marcasite are observed in the XRD pattern from the thermal CVD material, the most noticeable of which are at $2\theta = 33.0^\circ$ and $33.3^\circ$ corresponding to the pyrite (200) and marcasite (101) planes, respectively. However, the pattern is dominated by reflections at $2\theta = 30^\circ$, $33.8^\circ$, and $53.3^\circ$ which correspond to the $( \bar{1} 2 2 )$, (004) and $( 5 2 2 )$ planes of pyrrhotite ($\text{Fe}_{1-x}\text{S}$, $x = 0 – 0.2$). Another strong reflection for pyrrhotite is expected for the (040) plane at $43.2^\circ$, which suggests that the pyrrhotite displays a preferred crystal orientation. The thermal CVD XRD pattern in Fig. 3.5a is similar to the one reported by Schleich and Chang [25], who also used IPC
as the metal precursor for pyrite CVD. In contrast, under the same process conditions with pulsed-PECVD, non-stoichiometric compounds are no longer present and only pyrite and marcasite signals were observed. The pulsed PECVD film at 240 °C also had both marcasite and pyrite phases detected by XRD, but the marcasite fraction was the greatest at 380 °C where thermal CVD contributes to growth. This trend was supported by the Raman spectra in Figure 3.5b. Below the critical temperature the strongest intensity is from the vibrational modes of pyrite, whereas the marcasite band at 326 cm\(^{-1}\) dominates the spectra at \(T_s > T_c\). Though only weak reflections were observed by XRD, Raman displays signals that confirm the presence of pyrite and marcasite phases in the thermal CVD film. Note that pyrrhotite was not detectable because it is Raman inactive [45]. These results clearly demonstrate the benefits of plasma processing. Thermal CVD favors formation of marcasite and Fe\(_{1-x}\)S phases, while the addition of plasma eliminates Fe\(_{1-x}\)S and enables operation at lower substrate temperatures to reduce the marcasite fraction.

![Figure 3.5: Comparison of (a) XRD patterns and (b) Raman spectra from thermal CVD and pulsed PECVD films at selected temperatures.](image)
3.5.3 Plasma Power and Optical Properties

The final variable explored was plasma power, which was varied from 15 – 100 W with the substrate temperature and duty cycle fixed at 240 °C and \( \tau = 0.67 \), respectively. Figure 3.6a shows the spectra collected by OES at different RF power. The strong bands between 300 - 600 nm are associated with emission from sulfur dimers while the emission lines between 650 - 850 nm are associated with argon. Weak peaks associated with Fe and CO+ at 375 nm and 428 nm, respectively, were observed in IPC/argon plasmas, but these were no longer distinguishable when H\(_2\)S was added. Previous studies of H\(_2\)S/Ar mixtures in an inductively coupled plasma have shown a strong peak for atomic hydrogen at 656 nm [40], and we expected to see this peak if atomic hydrogen attained a significant density in the plasma. While this peak was observed, it was negligible relative to the emission from sulfur dimers and argon. As the RF power was increased, the overall plasma intensity increased as expected. The intensity ratio of the dominant

![Figure 3.6: (a) OES spectra obtained from H\(_2\)S/Ar/IPC plasmas and (b) growth per cycle as a function plasma power for films deposited at \( T_s = 240 \) °C and \( \tau = 0.67 \).](image-url)
sulfur-related peak (420 nm) relative to the argon peak at 750 nm gradually increased from 0.26 - 0.59 as plasma power was increased from 10 - 75 W, and sharply increased to 1.7 as power was further increased to 100 W. This suggests that the level of H₂S dissociation and thus sulfur activity scales with RF power. Figure 3.6b shows the relationship of deposition rate with plasma power. Increasing the power caused a decrease in deposition rate between 15 – 75 W, with a sharp drop off in rate between 75 W to 100 W. The decrease in rate was attributed to increased gas-phase consumption of IPC derived precursors, and which coincides well with the trends observed by OES.

Figures 3.7a and 3.7b shows both XRD and Raman characterization of films deposited as a function of plasma power. Both display the interesting finding that the fraction of the marcasite phase increases with plasma power. At 15 W, marcasite was not detectable by XRD and only as a small shoulder at 326 cm⁻¹ was observed with Raman. This condition produced the most phase pure pyrite within the range of all process parameters tested. This finding was somewhat counter-intuitive. As shown above, increasing plasma exposure time through increasing duty cycle (Fig. 3.2) was found to be beneficial for the pyrite component. Likewise, the presence of plasma mitigated impurities produced through thermal CVD (Fig. 3.5). One plausible explanation for this trend is that the sulfur species (S, S₂) generated by plasma activation of H₂S are beneficial for forming FeS₂, but that excessive exposure to the other excited species generated by the plasma such as electrons, ions or atomic hydrogen may be detrimental to pyrite formation. The bombardment and/or recombination of these species on the growing surface may induce damage or lead to localized heating. This would be consistent with our earlier observations that higher substrate temperature favored marcasite.
Lastly we examined the optical characteristics of all the films produced in this work. Figure 3.8 displays optical properties of a representative selection of films. These samples include a thermal CVD film, as well as pulsed PECVD films with varying pyrite:marcasite ratios. Figure 3.8a shows spectra representative of pulsed PECVD films, which was obtained at 50 W, $T_s = 240$ °C, and $\tau = 0.67$. All pulsed PECVD films displayed a high level of reflection near 50%. Reflection-corrected absorption coefficients are plotted as a function of photon energy in Figure 3.8b. Despite significant variation in phase purity, the pulsed PECVD films all displayed very similar properties with absorption coefficients of $\sim 10^5$ cm$^{-1}$ for $h\nu > 1.5$ eV, regardless of the process conditions. Thermal CVD films are not included as they did not show any band edge or features expected of a semiconductor. The optical band gap was extracted assuming an indirect transition, as shown in the plot of $(\alpha E)^{1/2}$ versus photon energy. As shown in Figure 3.8c, the optical band gap was estimated by the intersection of the two linear regions of these curves. Fig. 3.8c also includes the analysis of a thermal CVD film, which is the horizontal line with no specific absorption features. For all FeS$_2$ films the indirect band gap was determined
to be $1.06 \pm 0.03$ eV, independent of pulsed PECVD process conditions. The band gap values are consistent with the range of indirect band gaps reported in previous pyrite studies of $0.9 - 1.1$ eV [20, 26, 29]. Our results are also consistent with the Law group [30] in that neither the band gap nor the absorption coefficients are appreciably impacted by the ratio of pyrite to marcasite. Recent DFT calculations suggested that marcasite has a band gap no less than pyrite [46], and the findings here support that assertion.

Figure 3.8: (a) Representative transmission spectrum from a film produced at $T_s = 240$ °C, $\tau = 0.67$ and 50 W. (b) Plot of absorption coefficient versus photon energy from selected films. (c) Tauc analysis of indirect optical band gap from selected films.
3.6 Conclusions

We have demonstrated self-limiting growth of stoichiometric FeS$_2$ thin films through pulsed PECVD using IPC and H$_2$S. This technique produces uniform films with thicknesses that can be controlled with angstrom level resolution. Substrate temperatures must be < 300 °C to eliminate contributions from thermal CVD which produce substoichiometric compounds, but also greater than 150 °C to prevent sulfur condensation. The growth per cycle could be adjusted from 0.1 – 1 Å/pulse through control of plasma power and/or duty cycle. Pulsed PECVD produced stoichiometric FeS$_2$ without the need for post deposition annealing, and the films contain a mixture of pyrite and marcasite phases. The relative amounts of these two phases could be adjusted through process conditions, and the most phase pure pyrite was produced at a combination of low RF power, high duty cycle, and low temperature. All pulsed PECVD films display optical band gaps (~1 eV) and absorption coefficients ($\alpha$ ~ $10^5$ cm$^{-1}$) that are consistent with previous reports for FeS$_2$, and these values were insensitive to the pyrite:marcasite ratio in the films. The use of plasma provides significant advantages over conventional thermal CVD, though the results also suggest that excessive exposure to high energy species may favor the formation of the marcasite phase. Further studies are underway to explore the optoelectronic performance of these materials.
FeS$_2$ thin films were deposited by pulsed plasma enhanced chemical vapor deposition (PECVD). Deposition parameters of duty cycle, plasma power, and substrate temperature could be used to control crystal phase. By tuning these parameters, both pyrite and marcasite rich films were deposited and explored for potential applications in sustainable energy. The optoelectronic properties were examined as a potential absorber for photovoltaics. The relative photoconductivity of pyrite, 11%, was more than marcasite, 6%, but solid-state devices fabricated with pyrite showed no photo response or rectifying behavior. Pyrite was tested as a cathode for Li ion batteries and showed initial discharges near 890 mA*hr/g. Similar capacities were observed initially for marcasite, but films degenerated after a few cycles.

4.1 Introduction

Pyrite, cubic FeS$_2$, is a promising material for energy applications. It has invoked renewed interest as an absorber layer for photovoltaics because it has a strong absorption coefficient (10$^5$ cm$^{-1}$), suitable band gap (~1 eV), and consists of earth abundant Fe and S [5]. The group at Hahn-Meitner-Institut proposed an efficiency target of 18.5% based upon available optoelectronic properties of pyrite [8]. Actual device results have fallen far short of this target. The best device performance was a photo-electrochemical cell reported at <3% [7]. Solid state devices have been largely unsuccessful. Device configurations explored have included Schottky diodes with Au, Ni [47], Pt [48], and Al metals, CuInSe$_2$ (CIS) based structures, depleted heterojunctions, and hybrid organic devices [9]. Schottky diodes and CIS based structures were
tested by the Korgel group, who deposited pyrite layers by spray and dip coating of synthesized inks [9], but the devices had negligible photo responses and either no or non-ideal rectifying behavior. One explanation proposed for the poor performance was the difficulty of controlling stoichiometry of pyrite, which was reported at 1.9:1 S:Fe. Other potential causes for the poor performance of pyrite include marcasite (orthorhombic FeS2) impurities [11], and Fermi-level pinning from surface defects [7, 20].

Pyrite is also attractive as a potential cathode material for Li ion batteries because of its high theoretical specific energy (~1300 Wh/kg). It has been used commercially as a primary battery since the 1990’s [12] and research for pyrite has focused on improving its rechargeability [49] and developing microbatteries for microelectromechanical systems (MEMS) [14]. Techniques used to make the pyrite cathode include solution synthesis [50], ball milling/solid state reaction [51], slurry coating Al electrode [52], and embedded microspheres [53]. The first discharge for Li-FeS2 have been reported up to ~ 840 mAh/g, near maximum theoretical capacity, but significant declines in storage capacity are observed after > 25 recharging cycles to 300 - 400 mAh/g [54, 55].

We have previously introduced pulsed-PECVD as a new technique for self-limiting growth FeS2 thin films [56]. This technique enables digital control over film growth, ~1 Å/pulse. The self-limiting mechanism produces an in situ annealing step that enables stoichiometric FeS2 to be deposited each pulse. Pulsed-PECVD has been shown to deposit stoichiometric FeS2 at substrate temperatures between 200 – 400 °C without the need for post-deposition annealing, while thermal CVD resulted in sub-stoichiometric pyrrhotite. Films were of a mixture of pyrite and marcasite and the ratio of these two phases could be tuned by controlling duty cycle (τ), substrate temperature (T_s), and plasma power. The onset of thermal CVD, T_c, was identified at
300 °C, and above this temperature thermal CVD will occur during the plasma off-time portion of each pulse. The marcasite fraction was found to increase at $T_s > T_c$ while pyrite was favored at $T_s < T_c$. Increased duty cycle ($\tau \geq 0.67$) and reduced power, $\leq 30$ W, was also found to increase the pyrite fraction while lower duty cycle and increased power favored marcasite.

In this study, pulsed-PECVD was used to deposit pyrite rich and marcasite rich FeS$_2$ thin films. These films were then used to examine the optoelectronic properties as well as its performance as a cathode for Li-ion batteries. The goal was to determine if the properties were phase-dependent.

### 4.2 Experimental

The following two sections describe the techniques used to fabricate devices and the methods used for characterization.

#### 4.2.1 Device Fabrication

Precursors used for depositing FeS$_2$ films were iron pentacarbonyl, Fe(CO)$_5$ (99.5%, Strem Chemicals) and H$_2$S (Air Liquide), both diluted in argon. Deposition parameters are summarized in Table 4.1 and additional details of the pulsed-PECVD experimental setup are provided elsewhere [56]. Schottky diodes were produced first by depositing FeS$_2$ films onto FTO coated glass (TEC 15) and completed by evaporation of metal (Au, Cu, Al) dots with ~75 nm thickness and 11 mm diameter. A fourth device structure was a solid state heterojunction produced by depositing FeS$_2$ onto 100 nm CdS on FTO. Gold dots were evaporated onto FeS$_2$ and served as back contacts.
Table 4.1: Summary of the baseline conditions discussed in this work.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>95% Pyrite</th>
<th>85% Marcasite</th>
<th>50:50 Pyrite:Marcasite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plasma off time (s)</td>
<td>1</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>Plasma on time (s)</td>
<td>2</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Duty Cycle ($\tau$)</td>
<td>0.67</td>
<td>0.20</td>
<td>0.67</td>
</tr>
<tr>
<td>Substrate Temperature (°C)</td>
<td>200</td>
<td>240</td>
<td>400</td>
</tr>
<tr>
<td>RF Power (W)</td>
<td>25</td>
<td>50</td>
<td>25</td>
</tr>
<tr>
<td>IPC Flowrate (sccm)</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>$\text{H}_2\text{S}:\text{IPC Ratio}$</td>
<td>36</td>
<td>36</td>
<td>36</td>
</tr>
<tr>
<td>Pressure (mTorr)</td>
<td>400</td>
<td>400</td>
<td>400</td>
</tr>
</tbody>
</table>

4.2.2 Characterization

Raman spectroscopy was performed using a WITech Alpha 300R Confocal Raman Microscope at an excitation wavelength of 532 nm and 100X magnification. Field emission scanning electron microscope (FE-SEM), model JEOL JSM-7000F, was used to image the cross-section of films deposited on silicon. I-V measurement of devices were performed using a probe station under dark and AM 1.5 illumination. Conductivity was measured on films deposited on non-conductive glass using a 4-point probe. Photoconductivity was measured by illuminating films with a Cole-Parmer Instrument Fiber Optic Illuminator, Model 41500-50, positioned ~2 cm from the film and measuring the change in sheet resistance with a 4-point probe.

For battery testing, ~300 nm films were deposited onto FTO coated glass. The electrochemical performance was determined by performing cyclic voltammetry (CV) at a 0.1 mV/s scan rate and discharge-charge at constant current using a BioLogic VMP3 multichannel potentiostat. The exposed sample area was 1 cm². All samples were examined using a two-electrode geometry with Li metal serving as both the counter and reference electrode. The electrolyte was 1 M Li perchlorate dissolved in propylene carbonate, and all testing was conducted in an inert atmosphere.
4.3 Results and Discussion

The first section describes the deposition and characterization of pyrite and marcasite rich films. The second part characterizes the optoelectronic properties of these films for photovoltaics and the last section evaluates films as a potential cathode for Li ion batteries.

4.3.1 Film Deposition

Figure 4.1a displays representative Raman spectra for pyrite and marcasite rich films. Both films contained mixtures of marcasite, identified by the Ag mode at 326 cm<sup>-1</sup>, and pyrite, identified by the Eg and Ag modes at 343 cm<sup>-1</sup> and 377 cm<sup>-1</sup>, respectively. The area for the Ag modes were integrated to provide estimated composition, though this is for relative comparison only as Raman is not an accurate tool for quantifying mass fraction. While X-ray diffraction was also used to characterize films, Raman spectroscopy has been shown to be the most sensitive technique for identifying marcasite [26]. To maximize the pyrite phase, the duty cycle was set sufficiently high (τ = 0.67), the plasma power was low (25 W), and the temperature was set to 200 °C. We found that lowering the temperature further from 240 °C down to 200 °C had the furthest reduction of the marcasite shoulder at 325 cm<sup>-1</sup> (~95% pyrite). This might be caused by an increase in the sticking coefficient of S* at lower temperatures. Temperature could not be lowered further because sulfur’s condensation point is ~180 °C. Marcasite rich film was produced at a low duty cycle, τ = 0.20, plasma power of 50 W and substrate temperature of T<sub>s</sub> = 240 °C. Raman spectra for this film is displayed in Figure 1a, which shows marcasite as the predominant phase, ~ 85%.

Films made by self-limiting growth display a uniform, homogenous nanocrystalline grain structure, shown in Figure 4.1b. Above the onset of thermal CVD (T<sub>с</sub> ≥ 300 °C), the process is
no longer self-limiting and thermal CVD will occur during the plasma off step. This growth leads to the morphology shown in Figure 4.1c, with larger, randomly oriented crystal grains. Larger crystal structure is preferable for photovoltaics and so films produced in this regime was of interest for determining the impact of crystal size on optoelectronic properties. Raman spectra of these films is shown in Figure 4.1d, which show that the marcasite phase is favored (~65%) with a corresponding plasma power of 50 W and duty cycle of $\tau = 0.67$. To try and increase the pyrite
phase, the plasma power was reduced from 50 W down to 25 W. This did reduce the marcasite fraction to ~50%, but the marcasite phase was still greater than those films produced at 200 °C. The film was then annealed at 400 °C with an H₂S/Ar plasma at 25 W, 400 mTorr for 4 hrs to try and further reduce the marcasite fraction, but no appreciable change was observed. The film deposited at Tₛ = 400 °C and 25 W was used to compare electronic properties with films deposited at Tₛ ≤ 240 °C.

### 4.3.2 Electrical Properties

Table 4.2 summarizes the conductivity of the three different films, measured by 4-point probe. Also included is a thermal CVD film produced at 380 °C that was substoichiometric, S:Fe = 1.7, and identified as primarily pyrrhotite by XRD. The thermal CVD film was very conductive, ~1000 S/cm and is representational of pyrrhotite’s metallic nature. Both marcasite rich and pyrite rich films deposited by pulsed-PECVD at Tₛ ≤ 240 °C have conductivities on the order ~10 S/cm, with marcasite being slightly more conductive than pyrite. Conductivity of pyrite films has been reported in the range of 10⁻⁶ – 10 S/cm [10, 20, 26, 32], with our films being near the more conductive limit. One reason for this high conductivity could be that the homogenous, polycrystalline film is dominated by surface defects that provide more carriers. The 50:50 marcasite:pyrite film deposited at 400 °C had a conductivity that was an order of magnitude lower, < 1 S/cm and consistent with its larger crystal size.

<table>
<thead>
<tr>
<th>Film</th>
<th>Conductivity (S/cm)</th>
<th>Relative photoconductivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrrhotite Film</td>
<td>~1000</td>
<td>--</td>
</tr>
<tr>
<td>95% Pyrite, Tₛ = 200 °C</td>
<td>6.4 ± 0.2</td>
<td>11%</td>
</tr>
<tr>
<td>85% Marcasite, Tₛ = 240 °C</td>
<td>11.6 ± 0.2</td>
<td>5%</td>
</tr>
<tr>
<td>50:50 Marcasite:Pyrite, Tₛ = 400 °C</td>
<td>0.7 ± 0.1</td>
<td>6%</td>
</tr>
</tbody>
</table>
To explore the optoelectronic properties, the relative change in conductivities was measured under intense illumination. The results of these tests are shown in Table 4.2. Out of the three films, the ~95% pyrite film had the greatest increase in conductivity, ~11%. The ~85% marcasite film showed only a ~5% increase. The 50:50 marcasite:pyrite film with large crystal size had 6% photoconductivity, similar to the marcasite rich film. This results would support that pyrite is a better photo-absorber than marcasite in that purity of the crystal phase was more important than crystal size. However, even 11% is well below the desired photoconductivity of an absorber material for photovoltaics. Photo-conductivity for pyrite has been reported at ~100% under AM 1.5 [20, 32], much greater than our films which were exposed to greater illumination.

The electronic properties were also explored by making simple devices using pyrite as an absorber layer. The basic device structure was to create Schottky diodes using metal/semiconductor structure on a FTO substrate. The three metals tested were Au, Cu, and Al. If the film is n-type, than Au would be expected to make the best diode due to its large work function. Alternatively if the film is p-type, Al would make the best diode as a low work function metal. Figure 4.2 shows I-V measurements of each film. None of the three metals show rectifying behavior and no photo-response when illuminated. Both and Au and Cu show low resistance, which was confirmed to be primarily the sheet resistance of the FTO film rather than resistance through the metal/FeS$_2$ junction. Part of this could be due to shunting from pinholes in the FeS$_2$ film. Schieck et al. [57] found Au and Cu to have non-linear behavior and used Pt as the best contact for low resistance, linear behavior. However, these films were made by CVT and were between 200 – 800 micrometers, ~1000 thicker than films in this study. Using the slope of the I-V curve as a worse case scenario, Au and Cu have an ohmic resistance $\leq 0.4$
Ohm-cm\(^2\). While these metals did not form a Schottky barrier, they would be promising for low resistance back contacts. Alternatively, the Al had an ohmic resistance of 5.7 Ohm-cm\(^2\) and would be less desirable as a back contact. Aluminum has been reported to have a high ohmic resistance for pyrite when compared to other metals [22, 57].

![Graph](image)

**Figure 4.2:** Current versus voltage measurement of metal/FeS\(_2\)/FTO and metal/FeS\(_2\)/Cd/FTO device structures

A p-n junction structure of Au/FeS\(_2\)/CdS/FTO, with ~100 nm pyrite was also tried. Figure 4.2 displays the I-V measurement of this structure. This device showed no rectifying behavior and had low resistance similar to the Au/pyrite and Cu/pyrite devices. The poor performance of this device structure is consistent with the findings of Steinhagen et al. [9], who found minimal photocurrent or rectifying behavior and no PV response.
4.3.3 Li-ion Batteries

The second application explored for FeS$_2$ was as a cathode material for Li-ion batteries. Cycle voltammetry was performed to understand reactions between Li and FeS$_2$. Anticipated reactions are the following:

\[
\text{Rxn 1: } \text{FeS}_2 + 2 \text{Li}^+ + 2 \text{e}^- \leftrightarrow \text{Li}_2\text{FeS}_2 \quad 1.5 \text{ V vs Li/Li}^+
\]

\[
\text{Rxn 2: } \text{Li}_2\text{FeS}_2 + 2 \text{Li}^+ + 2 \text{e}^- \leftrightarrow \text{Fe} + 2 \text{Li}_2\text{S} \quad 1.4 \text{ V vs Li/Li}^+
\]

\[
\text{Rxn 3: } \text{Li}_{(2-x)}\text{FeS}_2 + x \text{Li}^+ + x \text{e}^- \leftrightarrow \text{Li}_2\text{FeS}_2 \quad (0 < x < 0.8) \quad 2.0 \text{ V vs Li/Li}^+
\]

Figure 4.3a and 4.3b displays the results of CV cycles for ~95% pyrite and ~85% marcasite films, respectively. The numbers in the Figure correspond to the three reactions described above. For the first scan from 2.7 - 1 V, a small initial peak occurs at 2.0 V for pyrite and no peak at this voltage occurs for marcasite. While in subsequent cycles this peak might be associated with Rxn 3, the Li$_{(2-x)}$FeS$_2$ phase should yet not be present. Most studies do not show this peak for the first cycle [54, 58], but it did appear for Wang et al. [50] for one sample of FeS$_2$ deposited on Ni, though the reaction was not identified. This peak could be surface contamination or preliminary reaction/charging of the surface. The next cathodic peak occurs at 1.5 V for both pyrite and marcasite. A shoulder at 1.3 V for pyrite indicates two separate reactions. This 2nd peak may also exist for marcasite but may have too much overlap to distinguish separate reactions. The peak at 1.5 V and 1.3 V are attributed to Rxn 1 and Rxn 2, respectively, and the voltage at which these occur is consistent for FeS$_2$ [54, 58]. Using a Gaussian fit for the pyrite scan, the estimated proportion of area for the first (1.5 V) and second (1.3 V) peaks are 53% and 47%, respectively. The near equivalent area is good agreement with the 1:1 reaction stoichiometry of 2 e$^-$ per reaction. The anodic scan from 1.0 V to 2.7 V for both
pyrite and marcasite reveals a current peak at 1.9 V, which corresponds to the reverse of Rxn 2. The second peak at 2.6 V most likely corresponds to a combination of the reverse of Rxn 3, forming Li_{(2-x)}FeS_2, and the generation of elemental sulfur, because Rxn 1 is not reversible at ambient temperature [59].

Figure 4.3: Cyclic voltammetry for (a) ~95% pyrite and (b) ~85% marcasite rich films between 1.0 - 2.7 V at a scan rate of 0.1 mV/s. Labels 1 - 3 are assigned to reactions as numbered in the text.

During the second cathodic scan from 2.7 - 1 V, a peak for both films occur at 2.0 V, corresponding to Rxn 3 and the presence of Li_{(2-x)}FeS_2. Both films also display a 2nd cathodic peak at 1.4 V, which is ~42% of the area from the 1st scan. This reaction should primarily be Rxn 2 and not Rxn 1. During the cathodic scan of the 2nd cycle, peaks again occur 1.8 V and 2.6 V for pyrite, corresponding to the reverse of Rxn 2 and Rxn 3. The areas of both peaks are less than the first cycle, but the peak at 2.6 V is greatly diminished. Marcasite was different, where the current at 1.8 V was greatly diminished and no peak at 2.6 V. Current density was minimal for marcasite after the 2nd C-V cycle and inspection of the sample showed no film on the
substrate. The degradation did not occur for the pyrite film, where the 3rd – 5th cycles continue with similar features as the 2nd cycle, and slightly declining current density. Both marcasite and pyrite have similar 1st cycle C-V, but pyrite may be more robust through multiple charges.

The ~95% pyrite and ~85% marcasite films were also tested for charge - discharge capacity. Figure 4.4a and Figure 4.4b displays the discharge and charge curves for 6 cycles for the pyrite and marcasite films, respectively. It should be noted that the marcasite film was tested at higher discharge rate, 670 mA/g compared to 107 mA/g for pyrite, to be able to test more cycles and limitations of cycle-time resulted in only partial discharges. The first discharge for pyrite had a capacity of >1000 mA*hr/g for voltage between 2.6 – 1.5 V, which is more than the theoretical max of 890 mA*hr/g. A small plateau appeared at 2.2 V and most current was observed at 1.6 V. The short plateau at 2.2 V is typically not observed for FeS$_2$ during the first cycle [54, 58], but it does correspond to the unexpected peak for this film during CV (Figure 4.3a). The additional current generated by the reaction at 2.2 V could explain why the total capacity was > 890 mA*hr/g and may indicate a reaction unrelated to Li-FeS$_2$. The first

Figure 4.4: Characterization of discharge and charge cycles for (a) pyrite at 107 mA/g and (b) marcasite-rich films at 670 mA/g for 6 cycles of discharge
discharge of the marcasite film shows a rapid drop in voltage and plateau between 1.5 - 1.6V and no feature at 2.2 V was observed. Subsequent cycles show current plateaus from Rxn 2 at 1.5 V and Rxn 3 at 2.0 V. Both pyrite and marcasite has similar relative rate loss, ~30% after 6 cycles, and only small differences from the 3rd - 6th cycle. This is similar to other FeS₂ studies that have reported initial discharges between 700 - 840 mA*h/g and capacity losses of 30% or greater after the 6th cycle [54, 58]. Only marcasite was tested beyond 6 cycles, and by the 10th cycle, the film was completely degraded and delaminated from the FTO, similar to CV testing.

4.4 Conclusions

Both pyrite and marcasite rich films deposited at Tₛ < Tₑ display conductivity ~ 5 - 10 S/cm, while films deposited at Tₛ > Tₑ were an order of magnitude lower (~ 1 S/cm), which may be due to the larger crystal size. The metal/FeS₂ and CdS/FeS₂ structures showed neither rectifying behavior nor photo-response. Both Au and Cu showed minimal ohmic resistance. One potential cause for pyrites poor performance for PV is that the material is dominated by surface defects. Given, the high conductivity of the films and small crystal size, these films may be behaving degenerately doped due to an abundance of surface states regardless of stoichiometry and crystal phase. The ~95% pyrite films displayed slightly higher photo-conductivity, but even these films showed only ~11% increase under intense illumination. Pyrite as a cathode for Li-FeS₂ had promising results. First discharge was achieved theoretical capacity of ~890 mA*h/g and retained 70% of capacity for the after 6 charging cycles. Marcasite had similar initial performance but quickly degraded after only a few cycles.
Stoichiometric, highly oriented WS$_2$ thin films were deposed by pulsed plasma enhanced chemical vapor deposition (PECVD) using W(CO)$_6$ diluted in excess H$_2$S and argon. Pulsing transients induced higher plasma intensity than continuous-wave PECVD, and crystal quality and orientation could be tuned by plasma power and duty cycle. The best crystalline quality was achieved at combinations of high plasma power and intermediate duty cycles ($\tau = 0.50 - 0.67$). Films produced at these conditions displayed preferential orientation with WS$_2$ layers parallel to the substrate. However this condition was limited to films with thicknesses < 90 nm, and orientation changed to perpendicular to the substrate as thickness increased. Films were catalytically active for hydrogen evolution, and perpendicular orientation was shown to reduce the over potential to 240 mV vs. RHE.

5.1 Introduction

Tungsten disulfide is an emerging 2-D nanomaterial and is of interest for a multitude of applications. Like MoS$_2$, it forms nanosheets with a hexagonal crystal structure of S-(Mo/W)-S sandwich layers. Its 2-D nature makes it similar to graphene and is therefore being explored for related applications [60]. Weak Van-der-Waals forces between each layer provide excellent lubrication properties. It is a semiconductor that offers potential advantages to heterojunctions for applications such as photovoltaics [61, 62] because each layer is self-terminated without dangling bonds that can cause recombination and Fermi level pinning. Conversely, the edges of
the sheets are catalytically active and WS$_2$ therefore finds use as an industrial catalysis [63] and is being studied for water splitting [64-66].

A variety of techniques have been explored for depositing WS$_2$ films. Techniques for synthesizing single or few layers have involved evaporating WO$_3$ and exposing to sulfur in extreme temperature, $\sim$800 °C [67, 68], or first depositing a film such as W and then annealing in sulfur at $\sim$800 °C [69]. Techniques such as sputtering [70] and chemical vapor deposition (CVD) [71, 72] have been studied for making WS$_2$ nano-particles [60, 73] and thin films [71, 72]. Sputtering is performed with W targets in reactive H$_2$S/Ar plasma [70], while thermal CVD has explored using tungsten carbonyl, W(CO)$_6$, in an H$_2$S/Ar [71, 72] or elemental sulfur [73] atmosphere.

In this study, we demonstrate pulsed-PECVD for producing WS$_2$ thin films. In this technique, plasma is pulsed using square wave modulation at low frequency ($\sim$1 Hz). The technique was first demonstrated for depositing metal oxides [36, 38, 39, 74] with the advantages of producing uniform, high quality coatings at lower thermal budget compared to conventional thermal CVD but with faster net deposition rates than atomic layer deposition (ALD). The technique offers different deposition mechanisms that can provide advantages when compared with thermal CVD, CW-PECVD, or ALD [37]. We have recently demonstrated pulsed-PECVD for the synthesis of high quality, FeS$_2$ thin films utilizing iron carbonyl (Fe(CO)$_5$) in an H$_2$S/Ar plasma [56]. In this study, we apply the same principles by simply replacing Fe(CO)$_5$ with tungsten carbonyl, W(CO)$_6$. We explore parameters including precursor flow rate, plasma duty cycle ($\tau$), RF power, pressure and substrate temperature ($T_s$). We compare these films with those produced by thermal CVD and CW-PECVD under similar conditions. We describe the growth, quality, morphology and crystal orientation using a suit of
characterization techniques including Raman, XRD, FESEM, and EDAX. We then test their potential for use as an electrocatalyst for the hydrogen evolution reaction (HER) and show that controlling orientation can improve this process.

5.2 Experimental

The deposition chamber consisted of capacitive-coupled parallel plate reactor. Plasma was generated by 13.56 MHz RF source and a custom matching network was used to minimize reflected power. Precursors were pre-mixed and delivered to the chamber through a 13.9 cm diameter showerhead, which also served as the powered electrode. Flow of W(CO)$_6$ (99.5% Strem Chemicals) was controlled using a bubbler [41] controlled to 450 Torr, and the argon carrier gas flowrate was set to 32 sccm using an mass flow controller (MFC). The temperature of the bubbler, $T_b$, was set tested at 80 °C and 70 °C to achieve W(CO)$_6$ flow rate of 0.21 and 0.10 sccm, respectively. Hydrogen sulfide gas diluted to 10% in argon (Air Liquide) was controlled by an MFC set to 150 sccm. A third stream of argon set to 100 sccm was used to raise the reactor pressure to 400 mTorr. Table 5.1 summarizes the baseline conditions and parameter spaced explored in this work.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Baseline</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Duty Cycle ($\tau$)</td>
<td>0.67</td>
<td>0 – 1</td>
</tr>
<tr>
<td>Substrate Temperature (°C)</td>
<td>400</td>
<td>320 – 425</td>
</tr>
<tr>
<td>RF Power (W)</td>
<td>100</td>
<td>30, 100</td>
</tr>
<tr>
<td>W(CO)$_6$ Flowrate (sccm)</td>
<td>0.21</td>
<td>0.10, 0.21</td>
</tr>
<tr>
<td>W(CO)$_6$ partial press ($p_W$, mTorr)</td>
<td>0.30</td>
<td>0.30, 0.60</td>
</tr>
<tr>
<td>W(CO)$_6$ concentration, ($c_W$)</td>
<td>0.074%</td>
<td>0.037%, 0.074%</td>
</tr>
<tr>
<td>H$_2$S: W(CO)$_6$ Ratio</td>
<td>71</td>
<td>Fixed</td>
</tr>
<tr>
<td>Pressure (mTorr)</td>
<td>400</td>
<td>400, 800</td>
</tr>
</tbody>
</table>
Substrates consisted of silicon (100) wafers and fluorine doped tin oxide (FTO) coated glass (TEC 15, Hartford Glass), and had a nominal size of 3.5 cm X 3.5 cm. The native oxide of the silicon was removed by dipping in 2% HF and FTO glass was sonicated for 5 min in Alconox solution, then sequentially rinsed with DI water, acetone, and methanol. Substrates were attached to the grounded electrode located 5.7 cm above the showerhead. Substrates were heated with a resistance heater and temperature monitored with a thermocouple located outside of the reactor. An optical emission spectrometer (OES) was attached to the outside of the reactor to monitor the plasma emission spectrum through a site glass. Details of the reactor are provided elsewhere [42].

Raman Spectroscopy was performed using a WITech Alpha 300R Confocal Raman Microscope at an excitation wavelength of 532 nm and 100X magnification. Analysis was performed on films deposited onto silicon and spectra were centered to the 520 cm\(^{-1}\) silicon peak. X-ray diffraction was performed on films deposited on silicon substrates with a Siemens D500 diffractometer using Cu K\(\alpha\) (\(\lambda = 1.54\) Å) X-ray source. Absorption coefficients were calculated from transmittance measured using a Cary 5G UV-Vis-NIR photospectrometer, which was corrected for background and reflectance. Field emission scanning electron microscope (FE-SEM), model JEOL JSM-7000F, was used to image the top of films and to measure cross-section thickness. An energy dispersive X-ray analysis (EDAX) unit attached to the FESEM was used to determine the ratio of W and S. EDAX was measured using a 5 kV accelerating voltage and was calibrated to a WS\(_2\) standard (Ted Pella). Transmission Electron Microscope (TEM) images were performed using a Philips (FEI) CM200 TEM. Samples for TEM were prepared by scraping powder off the substrate and dispersing into ethanol, which was then deposited onto a copper grid. Polarization curves were measured using Gamry PCI4 Potentiostat at a scan rate of
5 mV/s. Films deposited on FTO coated glass served as the working electrode with a Pt mesh used as a counter electrode. The electrolyte was 0.5 M H₂SO₄ and a Ag/AgCl electrode served as a voltage reference. Voltage was correct for pH and reported versus the reversible hydrogen electrode (RHE). The onset potential was determined by first fitting current density data between 0 and -0.05 V vs RHE to a linear plot. The voltage at which measured current density was greater than 0.5 mA/cm² from the linear plot reported as the onset over potential.

5.3 Results and Discussion

The first five sections discuss the results of key process parameters for the deposition of WS₂ thin films. The last section explores film thickness and shows how this affects the electrocatalytic behavior for hydrogen evolution.

5.3.1 Precursor Delivery

The first objective was to determine the W(CO)₆ source temperature that would sufficiently supply enough vapor to deposit a film. The temperature was initially tested at 70 °C and 80 °C, which corresponds to W(CO)₆ flow rate of 0.10 and 0.21 sccm, respectively. Reactor conditions were fixed reactor at Tₛ = 400 °C, 400 mTorr, 100 W, and a duty cycle of τ = 0.67 (1 sec on, 2 sec off). Both temperatures produced a film and while it was anticipated that Tₘ = 80 °C would have a higher growth, instead the growth rates for both films were similar, ~0.7 Å/pulse. Films were characterized first by Raman, with spectra displayed in Figure 5.1a. Both films were identified as WS₂ by the two dominant modes, the E₂g¹ mode at ~352 cm⁻¹ and A₁g mode at ~419 cm⁻¹ [62, 75], and no other phases were observed. Films were then further characterized by XRD. Figure 5.1b displays the XRD patterns of these two films. The film deposited at Tₘ = 80
°C had a strong reflection at 14.4°, which is identified as the (002) plane for WS₂. Two additional, overlapping reflections at 32.8° and 33.6° were identified, corresponding to the WS₂ (100) and (101) planes. However, these two reflections were much smaller than the (002) plane. The strong intensity of the (002) plane compared to the (100)/(101) planes indicate that the WS₂ sandwich layers are preferentially oriented parallel to the substrate (c-axis \perp). For simplicity, orientation of layers parallel to the substrate ((002) plane) will be refer to as C(=), and non-parallel orientations ((100) and (101) planes) we be referred as C(\parallel). The film deposited at

Figure 5.1: (a) Raman spectra and (b) XRD pattern for films produced at \(T_b = 70\) °C and 80 °C (c) FE-SEM image of the top of WS₂ film at deposited at \(T_b = 80\) °C, (d) plot of absorption coefficient versus photon energy for a representative film deposited at \(T_b = 80\) °C.
\( T_b = 70 \, ^\circ C \) had no reflection at 14.4°. There is a reflection at 33°, corresponding to (100)/(101) planes and supports the presence of WS\(_2\), though the poor signal to noise ratio is indicative of poor crystal quality or the presence of amorphous material.

The film at \( T_b = 80 \, ^\circ C \) was further characterized and the morphology is shown in the FESEM image presented in Figure 5.1c. The film is composed of narrow platelets that are \( \sim 50 \) nm in width. Similar morphologies for thin film WS\(_2\) have been reported by CVD and reactive sputtering studies [72, 76]. EDAX was used to determine that the S:W ratio of the film and it was found to be stoichiometric (2.0:1 \( \pm \) 0.1). Figure 5.1d displays the absorption coefficient of the film characterized by UV-Vis-NIR. The film has a strong absorption coefficient, which was greater than \( 10^5 \, \text{cm}^{-1} \) for \( E \geq 2.3 \, \text{eV} \). The film displays an excitonic feature at 2 eV and a subtle feature at 2.5 eV that is characteristic of WS\(_2\) [77]. For the rest of the experiments, the W(CO)\(_6\) flow rate was set to 0.21 sccm, given the preferred crystalline nature of the film as indicated by XRD and the suitable stoichiometry and absorption spectra.

### 5.3.2 Duty Cycle

Duty cycle was the next parameter explored, which was varied between \( \tau = 0.33 - 0.80 \) with fixed parameters of \( T_s = 400 \, ^\circ C \), 100 W, and 400 mTorr, and deposition time was set to produce film thicknesses near 50 nm. Thermal CVD and CW-PECVD was also tested at these conditions, which is equivalent to \( \tau = 0 \) and \( \tau = 1 \), respectively. Both thermal CVD and CW-PECVD resulted in film deposition and Figure 5.2a shows the Raman spectra of these compared to \( \tau = 0.67 \). All three Raman spectra show the two WS\(_2\) modes at \( \sim 352 \, \text{cm}^{-1} \) and \( \sim 419 \, \text{cm}^{-1} \) with no significant differences and no other phases detected. This similarity in Raman spectra was
observed for other duty cycles too. We found that XRD was most sensitive at distinguishing physical differences and if WS$_2$ was detected by XRD, the Raman spectra of the film appeared similar to those displayed in Figure 5.2a. Figure 5.2b shows the XRD patterns of films as a function of duty cycle. Both the thermal CVD and CW-CVD films and had WS$_2$ reflections for (002) and (100)/(101). A smaller reflection at $38.2^\circ$ was also observed, which corresponds to the (104) plane. The comparable intensities of (002) and (100)/(101) indicate a mixture of C(=) and C(||) orientations. In stark contrast are the films deposited by pulsed-PECVD at $\tau = 0.50$ and 0.67, which is dominated by C(=) orientation, and these display improved signal to noise that indicates better crystal quality. Also shown in Figure 5.2b are the XRD patterns for $\tau = 0.33$ and 0.80, which show reflections for WS$_2$, but with either a mixture of C(=)/C(||) or a preferred C(||). Duty cycle also affected growth rate. The deposition rate for $\tau = 0 - 0.33$ and $\tau = 0.80 - 1$ were $\geq 2$ nm/min. For $\tau = 0.50 - 0.67$, the growth rates was reduced to 1.5 - 1.7 nm/min ($\sim$0.7 Å/pulse), which may be in part responsible for the improved crystallinity.

Figure 5.2: (a) Raman spectra and (b) XRD patterns for films at duty cycle of $\tau = 0 - 1$. 

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5.3.3 Plasma Diagnostics

To further understand why pulsed-plasma for $\tau = 0.50 - 0.67$ produced unique crystal quality, an optical emission spectrometer (OES) was used to characterize the plasma. The primary emission from the plasma is composed of Ar lines in the range of 650 - 850 nm and $S_2$ bands between 300 - 600 nm, with no other chemical species distinguishable. Figure 5.3a show the transient behavior for two wavelengths: the strongest Ar line at 750 nm and the strongest of the $S_2$ band centered at 420 nm. In this scan, plasma ignition occurs at $t = 5$ sec. Between 5 - 10 sec the plasma is composed of only $H_2S$ and Ar and no $W(CO)_6$ is flowing to the reactor. At ignition, the plasma quickly stabilizes within ~0.5 sec. At 10 sec, $W(CO)_6$ is introduced to the plasma. The metal precursor has a profound effect, doubling the plasma intensity. The intensity then slowly decreases and it takes a full 5 seconds for the plasma to stabilize, notably this amount of time is greater than the typical plasma on time. When the plasma stabilizes at 15 sec, the intensity is still greater than in the plasma without $W(CO)_6$. The steady state plasma at $t \geq 15$ sec is representative of CW-PECVD. Figure 5.3b shows the plasma intensity of Ar under pulsed-PECVD at $\tau = 0.67$ (2 sec on, 1 sec off) with and without $W(CO)_6$. When the $W(CO)_6$ is not flowing, the intensity is relatively constant for the 2 seconds pulse. When $W(CO)_6$ is flowing, there is spike in plasma intensity at ignition followed by a decrease in intensity over 2 seconds. The plasma during each 2 sec pulse from Figure 5.3b is best represented on Figure 5.3a by the intensity between 10-12 seconds. This period of high plasma activity is sustained in a pseudo-steady state created by pulsing that cannot be maintained by CW-plasma.

There are two potential causes for the improved crystallinity and preferred orientation at $\tau = 0.67$. First, the plasma intensity is greatest immediately after ignition, and this could lead to better annealing of the film. Another possibility is that the gas phase is composed of transient
intermediate species, $W^*$, formed after during ignition that are not present in appreciable quantities under steady-state CW-plasma and enables deposition to occur under a different reaction pathway. The sulfurization of $W^*$ might be occurring partially in the gas phase rather than after it is deposited on the substrate.

Figure 5.3: Plasma intensity measured at 750 nm (Ar) and 420 nm ($S_2$) versus time for (a) plasma intensity at ignition, with and without $W(CO)_6$ and (b) pulsed plasma (2 sec, 1 sec off, $\tau = 0.67$) with and without $W(CO)_6$ at 100 W, 400mTorr, and of $T_s = 400 \, ^\circ$C.

5.3.4 Pressure and Plasma Power

The impact of pressure and plasma power were also explored with the duty cycle and temperature fixed at $\tau = 0.67$ and 400 °C, respectively. Power was tested at 30 W, with pressure set at the base condition of 400 mTorr. Figure 5.4 displays the XRD pattern and shows the reflection at 14.4° was still the stronger than at 33°, but the difference was not as significant as at 100 W. The reduced signal and peak broadening of 14.4° at 30 W when compared to 100 W indicate the film at lower power is less crystalline. The growth rate was still ~0.7 Å/pulse, similar to 100 W. Pressure was then explored at 800 mTorr with power set at base 100 W. The
result of increasing the pressure of plasma is more collisions, which increase density of energetic species but reduce their average energy. The XRD pattern from this experiment is shown in Figure 5.4. At 800 mTorr, the (002) and (100)/(101) reflections were of similar orders of magnitude. The growth rate for this condition was doubled to ~1.4 Å/pulse and may be partly contributing to the change in orientation. The increased growth rate at 800 mTorr versus 400 mTorr is most likely due to an increase in W(CO)₆ partial pressure, from \( p_W = 0.30 \text{ mTorr} \) to \( p_W = 0.60 \text{ mTorr} \), with W(CO)₆ concentration constant, \( c_W = 0.074\% \). An additional experiment at 800 mTorr was conducted by diluting with argon to maintain the partial pressure at \( p_W = 0.30 \text{ mTorr} \), and decrease the W(CO)₆ concentrations from \( c_W = 0.074\% \), down to \( c_W = 0.037\% \). This reduced the growth rate to ~0.6 Å/pulse. However, the XRD pattern of this film shows no distinguishable reflection at 14.4° and only a weak reflection at 33°. Reducing W(CO)₆

![XRD patterns at varied power, pressure and W(CO)₆ concentration. Base conditions were 400 mTorr, 100 W, \( p_W = 0.30 \text{ mTorr} \), and \( c_W = 0.074\% \). Deviations from these conditions are noted by each pattern.](image)

Figure 5.4: XRD patterns at varied power, pressure and W(CO)₆ concentration. Base conditions were 400 mTorr, 100 W, \( p_W = 0.30 \text{ mTorr} \), and \( c_W = 0.074\% \). Deviations from these conditions are noted by each pattern.
concentration also reduced the increased plasma intensity at ignition. The concentration of $\text{W(CO)}_6$ is an important parameter, which directly affects the plasma intensity and drives $\text{C(=)}$ orientation and improved crystallinity, while increasing power also contributes to these attributes.

5.3.5 Substrate Temperature

The last variable that was tested was substrate temperature, which was varied from 320 - 425 °C with duty cycle, pressure and power fixed at $\tau = 0.67$, 400 mTorr, and 100 W, respectively. A series of thermal CVD experiments within the same temperature range was also performed, which showed that the onset of thermal CVD occurs at 330 °C. For pulsed-PECVD at 320 °C, deposition is driven by the plasma only and no thermal CVD will occur during the plasma-off time. The impact of this on pulsed-PECVD experiments was most immediately seen by reduced growth rate, from 0.7 Å/pulse at 400 °C to ~0.4 Å/pulse at 320 °C. The XRD patterns for these films are presented in Figure 5.5a. As temperature was reduced from 400 °C down to 320 °C, the XRD spectra remained mostly unchanged with the reflection at 14.4° still dominant. These results contrast with films produced by thermal CVD by Chung et el. using $\text{W(CO)}_6$ and $\text{H}_2\text{S}$ precursors [72], where temperature was found to be the most important parameter for controlling film orientation. At higher temperature, 425 °C, films resort to a random orientation as the reflections for the (100)/(101) planes increased.

Interestingly, at this elevated temperature a residue was observed on the substrate after deposition. Imaging of the residue, shown in Figure 5.5b, revealed the presence of a nanopowder on the surface. The powder was confirmed to be stoichiometric $\text{WS}_2$ by EDAX. The mixed orientation of the powder most likely dominated the XRD patterns. TEM images of
Figure 5.5: (a) XRD spectra at various substrate temperatures (b) FE-SEM X-section image of film on Si deposited at 425 °C shows the bulk of the material as a nano-powder, (c) and (d) shows TEM images of the nano-powder.

The powder are shown in Figure 5.5c, revealing small crystallites that are between 5 - 20 nm in size. At larger magnification, Figure 5.5d, the image shows a layered, crystalline structure consistent with WS₂. Nanoparticles were of similar size and appearance as those made by Vollath and Szabo [60], who used a microwave plasma with the same precursors, W(CO)₆ diluted H₂S/Ar. Nano-particles in this study were produced at much lower temperature, as low as 160 °C, but also higher pressures, ≥ 7.6 Torr. The higher pressure would be more conducive
for gas phase reaction and nucleation and would explain why nanoparticles were produced at lower temperatures.

5.3.6 Thickness and HER

Films thicknesses were nominally deposited at ~50 nm to best compare the effects of reactor parameters. To determine the influence of thickness as a parameter, a series of films were deposited between 20 - 240 nm at $\tau = 0.67$, 100 W, $T_s = 400 \, ^\circ C$, and 400 mTorr. XRD for these films are displayed in Figure 5.6a. The dominant reflection at 14.4° for film thicknesses between 20 - 90 nm show that C(=) continue as the preferred orientation in this range. As thickness was further increased to 160 and 240 nm, the orientation changed to a non-parallel orientation, C(∥). Figure 5.6b depicts an image of the 240 nm film, which shows a high density of platelets oriented upwards with larger feature sizes than when it was first nucleated (Figure 5.1c). Figure 5.6c is an image of the 89 nm film, which shows a morphology between 22 nm (Figure 5.1c) and 240 nm. [72]. Similar observations of transition from C(=) to C(∥) orientation with increased film thickness have been observed for reactive sputtering of WS$_2$ [70] and thermal CVD of WS$_2$ [72] and MoS$_2$ [78]. As defects form, growth occurs non-parallel to the substrate and growth is accelerated along the edge portion of the planes [72].

Films deposited on FTO from the thickness series were tested for a potential application as an HER catalyst, to determine the influence of orientation on the onset potential. Polarization curves for these different films are shown in Figure 5.6d and are compared to Pt and FTO, which serve as highly active and inert reference surfaces. The lowest over-potential to achieve hydrogen evolution was Pt, ~30 mV. For bare FTO, the over-potential was 550 mV and was reduced to ~340 mV with 20 nm of WS$_2$. The over-potential is further reduced to ~240 mV as
Figure 5.6: (a) XRD patterns of films at thickness between 20 - 245 nm. FE-SEM top view image of film at thickness of (b) 245 nm and (c) 89 nm. (d) polarization curves of the thickness series show current density of HER versus V vs. RHE

thickness increased to 240 nm and orientation changed from C(=) to C(∥). The active portion of WS₂ for catalyst is the edge sites, and an improvement in over-potential is most likely due to increase density of these sites. Best results for WS₂ HER onset over-potentials are between 100 - 200 mV [64-66]. One of the most successful techniques for exposing edge sites is multi-step, where after WS₂ is produced, it is then exfoliated to make nano-flakes and then depositing onto a substrate [64, 65]. The exfoliation process serves both to increase exposed edge sites and create lattice strain that increase activity. While the onset over-potential is greater for pulsed-PECVD, it
does produced electrocatalytic active surface for very thin films, < 300 nm, and demonstrates the potential benefit of orientation.

5.4 Conclusions

Stoichiometric, polycrystalline WS₂ films were successfully deposited by pulsed PECVD. Under pulsed operation the intensity of the plasma is significantly greater than under CW operation, particularly in the presence of W(CO)₆ precursor. The effective plasma intensity may be manipulated through control of duty cycle and an optimum range exists between $\tau = 0.50 - 0.67$ that was shown to improve crystallinity and produce films orientated parallel to the substrate. There are two parts of pulsing to consider. The first step, the plasma off-time (~1 sec) is set long enough to build up W(CO)₆ partial pressure before plasma ignition and short enough to minimize growth through thermal CVD. The second step, the plasma on-time (1-2 sec) is set to fully utilize the high intensity state created immediately after ignition and not too long to have the plasma intensity decline to steady-state CW-plasma. This window was sensitive to pressure but not substrate temperature, further supporting the importance of the plasma. Lastly, the control of orientation depends on film thickness. Above ~90 nm, defects led to the formation of platelets perpendicular to the surface. The parallel orientation is expected to be desirable for lubrication, whereas the latter improves the catalytic properties. Substrate temperature was also important. The threshold for thermal CVD was found to be ~330 °C, but it did not strongly impact crystal orientation. Interestingly operation above $T_s = 400$ °C resulted in the production of WS₂ nanocrystals, 5-20 nm in size, caused by gas phase reaction and nucleation.
CHAPTER 6
CONCLUSIONS AND RECOMMENDATIONS

6.1 Summary

Deposition of stoichiometric FeS$_2$ and WS$_2$ thin films was accomplished by pulsed PECVD. For FeS$_2$, the onset of thermal CVD using Fe(CO)$_5$ and H$_2$S was identified at $T_c = 300 \, ^\circ$C. Below this temperature, self-limiting growth occurred and growth rate could be controlled 0.1 - 1 Å/pulse. Films were a mixture of pyrite and marcasite at $T_s < T_c$, and crystal phase could be tuned to produce pyrite rich films by setting the duty cycle to $\tau \geq 0.67$ and reducing plasma power to $\leq 30 \, \text{W}$. At $T_s > T_c$, deposition was no longer self-limiting and the marcasite fraction was observed to increase. Films displayed an optical band gap of $\sim 1 \, \text{eV}$ and absorption coefficient of $\sim 10^5 \, \text{cm}^{-1}$, ideal for solar absorbers. However, the conductivity of pyrite and marcasite films was quite high ($\sim 10 \, \text{S/cm}$) and the photoconductivity was poor for both pyrite (11%) and marcasite (5%). Simple Schottky and CdS heterojunction based devices were fabricated with pyrite films, but characterization showed no rectifying behavior or photoresponse. Pyrite films were tested as a cathode for thin film Li ion batteries and displayed near theoretical capacity. Similar initial performance was observed for marcasite, but films degraded after only a few cycles.

For deposition of WS$_2$, the best crystallinity was achieved at intermediate duty cycles ($\tau = 0.50 - 0.67$) and high plasma power over a temperature range of $T_s = 320 - 400 \, ^\circ$C. This was attributed in part to high intensity, plasma transients that were sustained in a pseudo-steady state by plasma pulsing and W(CO)$_6$ concentration. Films produced under these conditions initially had C($) orientation, but as thickness increased to $> 90 \, \text{nm}$, orientation changed to from C($) to
C(∥). Films were catalytically active for water splitting, and the shift to perpendicular orientation reduce the onset potential for hydrogen evolution from 340 mV to 240 mV vs RHE.

6.2 Conclusions

The deposition of FeS₂ and WS₂ by pulsed PECVD had interesting similarities and differences. The growth rates of both materials were similar, ~1 Å/pulse, using carbonyl flow rates of ~ 0.2 sccm. The onset of thermal CVD was similar, ~300 °C for FeS₂ and ~330 °C for WS₂, indicating a similar kinetic barrier for both mechanisms. The barrier is most likely controlled by the dissociation of H₂S, as IPC has been observed to degrade to iron powder at temperatures much lower than 300 °C. The plasma enabled deposition of films below the onset of thermal CVD due to its ability to dissociate H₂S and generate an abundance of atomic S. While deposition of FeS₂ was self-limiting, the deposition of WS₂ was not. CW-PECVD of WS₂ was achieved while for FeS₂ the IPC was sacrificially deposited before reaching the substrate.

The effect of plasma power was different for each material. For FeS₂, plasma exposure was important for converting marcasite to pyrite where the duty cycle had to be \( \tau \geq 0.67 \) to maximize the pyrite phase. While plasma exposure was good, the power had to be low, \( \leq 30 \) W, to minimize marcasite, which may be due to damage from ion bombardment or localized heating. Addition of either IPC or W(CO)₆ to the Ar/H₂S mixture resulted in significant increase in plasma intensity. The effect of the metal precursor is a fascinating phenomenon because it is present only in small concentrations, ~ 0.1%, yet it has a profound impact on species that make up > 95% of the gas phase, Ar and S. The effect of metal precursors to plasmas has been observed before, but the cause is not well understood [79]. For WS₂, the increased plasma intensity observed during plasma ignition was correlated with improved crystallinity. Setting the
duty cycle between $\tau = 0.50 - 0.67$ increased the partial pressure of W(CO)$_6$ at plasma ignition that created a state of higher plasma intensity than CW-plasma, and this improved the film quality and altered orientation. The increased energy of the plasma may improve annealing of the films which would be supported by the improved crystallinity and C(=) orientation observed from increased plasma power. Another possibility is that pulsing creates a deposition mechanism different from CW-PECVD.

As a solar absorber, pyrite does not appear to be promising. While marcasite and pyrite did not have apparent differences in optical band gap and absorption coefficient, pyrite had double photoconductivity than marcasite. However, the photoconductivity increase was relatively minor. This may be due to the small crystal size, where the film may be dominated by surface defects. The high conductivity of the pyrite film would support this. Interesting, the film deposited at $T_s > T_c$, which had larger crystal sizes and was less conductive also had less photocurrent than the pyrite film. This raises an interesting question that perhaps the marcasite phase is the bigger cause for the poor performance and not surface effects, at least for these films.

Pyrite displayed much more promise as a potential cathode for Li ion batteries. It had near theoretical capacity for the first discharge, and this may in partly driven by the stoichiometric control of the pulsed-PECVD and the use of thin, uniform films may improve Li diffusion. Marcasite looks to have similar performance, but the film quickly degraded after a few cycle. This is not a true "apples to apples" comparison because the discharge rate and number of cycles were different. However, cyclic voltammetry was performed under the same conditions. For CV, the current density of marcasite dropped off significant after the 1st cycle and completely degraded after the 2nd cycle, while only small decreases was observed for pyrite.
after 5 cycles. The marcasite crystal structure may not have been as conducive to Li intercalation as the pyrite structure, or the marcasite film may have had poor adhesion to the FTO.

While WS₂ is a 2-D material, its orientation in the third dimension can have implications to its properties. Orientation of C(=) would be beneficial for solid state heterojunctions. Studies that have used this orientation to make devices have synthesize their films at ~ 800 °C to achieve crystalline sheets [61, 62], and the ~ 50 nm crystal size produced in this study may not be practical for such applications. For electrocatalytics, reducing the basal/edge planes ratio may further promote HER activity [66]. This was accomplished in this study by increasing the density of edge sites through a one step deposition to form C(∥) orientation.

### 6.3 Recommendations

To further research of pyrite as a photo absorber, the photo-conductivity of the films would first need to improve. Potential causes of the poor performance could be the remaining marcasite phase (~5%) or the small crystal sizes. One potential way to eliminate these is to perform additional sulfur annealing to eliminate the marcasite phase and increase the crystal size. Those who perform sulfur annealing have not reported successful devices and using this technique on pulsed-PECVD films may still yield poor results. Why there may be interesting learning’s, the poor PV performance of pyrite films may indicate the pyrite is not as promising for PV as originally hoped and may not be worth pursuing.

Pyrite as a cathode may be more promising for research. Initial results are comparable with literature [54, 58]. The results reported represent only two films and additional testing would be required to validate this. Pyrite was only tested for capacity for 6 cycles, and testing
for at least 25 cycles may be necessary to compare its long-term life with other studies. Evaluating film thickness versus performance may also be an interesting study because thickness can be precisely controlled by pulsed-PECVD.

For WS₂, HER catalyst seems to have the most potential, as the small crystal size of WS₂ films does not seem appropriate for semiconductor applications. Further optimization studies could be performed to improve the onset potential. One approach is to optimize C(∥) and achieving this at smaller thickness. This could be done by depositing an initial layer at conditions that prefer C(∥) to expose edges for growth, then complete deposition using conditions that favor improved crystallinity (τ = 0.67, 100 W). The best results for HER have involved creating strain in films to improve activity. Preliminary testing through mild oxygen incorporation have shown improved HER, and this would be consistent with results produced for MoS₂ [80]. Evaluating substrates besides FTO may be necessary, as cycling WS₂ as a catalyst resulted in delamination of films. Another interesting area to explore would be creation of WS₂ nanoparticles. Increasing temperature is one parameter, while results of Vollath and Szabo [60] indicate using higher pressure and pulsing frequency may also benefit nanoparticle formation.

Another potential endeavor is to explore film deposition of MoS₂ by pulsed PECVD. The crystal structure and properties of MoS₂ are very similar to WS₂ and many studies compare these two side by side. Molybdenum carbonyl, Mo(CO)₆, is a common precursor for making MoS₂ and lessons from WS₂ deposition could be reapplied.
REFERENCES CITED


APPENDIX A
PULSED PECVD REACTOR SOP

Sample Preparation

1. Close Vacuum Pump valve
2. Slowly open Vacuum-Break valve to bring reactor to Atm pressure
3. Set aside heater and copper grounding, and remove reactor lid
4. Wipe out any residue with Kimwipes
5. Attached substrates to the top of the reactor lid using metal holders and Kapton tape.
   Place lid back on top of the reactor. (Figure A.1a)
7. Open Vacuum Pump valve and verify that vacuum is achieved by observing drop in pressure readout
8. Reattach Copper Ground using Clip (Note: best to wait until after low vacuum is achieved to do this)

Reactor Heat-up

1. Place heater onto the top of the reactor lid. Place thermocouple into the heater hole.
   Turn on the heater Variac and set Variac to desired setting for reactor conditions using heating curve (Figure A.1b). (Note: For repeat experiment at the same temperature, it is best to reference the Variac setting, as the thermocouple will vary +/- 15 °C)
2. Turn on heat tape to site glass to prevent sulfur condensation. Temperature controllers are marked: setting 4 for "OES", setting 8 for "Site Glass"
3. Wait for reactor to heat up (~1-2hrs)

4. Verify vacuum is okay with a leak test (typically ~20 mTorr/min)

**Prepare Ar and Precursor Gas Delivery**

1. Turn on Argon flow
   
a. Open manifold valve (V26)
   
b. Open Argon MFC Feed and Exit valves (V4 and V2), and Ar cylinder valve
   
c. Turn MFC controller to channel 2
   
d. Turn nob to “Manual – set”, set desired output (0 - 695 sccm), and turn nob to "Manual - flow" to verify flow

2. Set Bubbler Pressure and Flow
   
a. Make sure flow is setup for desired bubbler (upstream 3-way valve set, bubbler not in use is isolated)
   
b. If using W(CO)$_6$ bubbler, turn on bubbler heat tape (#1 set to 4.5, #2 set to Hi, #3 plug in)
   
c. Valves In and Out of bubbler should be closed, bubbler Bypass should be open
   
d. Open valves to flow Ar to bubbler (3-way Valve (V5), Valve V18, and MFC5 feed valve)
   
e. Turn MFC controller to channel 1
   
f. Turn nob to “Manual – set”, Set to desired flow rate (0 - 70 sccm), switch to “Manual - flow” to verify flow
   
g. Use needle valve to adjust bubbler pressure
   
h. Make sure Reactor Bypass 3-way valve is in the bypass position
i. Start flow through bubbler (Note: the following order of steps evolved for IPC to avoid liquid entrainment and plugging of tubing, the order is not as important for W(CO)₆)
   i. Close Bubbler bypass valve
   ii. Allow bubbler pressure to increase by 100-200 Torr, then open Bubbler Bypass Valve (Note: goal is to have pressure in tubing greater than bubbler)
   iii. Open Bubbler Outlet Valve and Bubbler Inlet Valve
   iv. Close Bubbler Bypass Valve
j. Allow 15 min of flow through bubbler before starting deposition to make sure flow is at steady state

Figure A.1: (a) Image of substrates attached to Reactor Lid. (b) Estimate of substrate temperature as function of Variac Setting

**Igniting Plasma and Starting Deposition**

1. Open Labview Program
   a. Open “Pulsed Power Supply Front End Rev. 1”
   b. Select “Run” and “Run Continuously” buttons in the top left hand corner
c. Set “Power Set Point”, “On Time”, and “Off Time” to desired settings

2. Open OOIBase 32 (OES software)

3. Turn on RF generator

4. Turn on secondary computer monitor

5. Start H2S flow
   a. Open "H2S" valve on manifold
   b. Turn MFC controller to channel 3
   c. Turn nob to “Manual – set”
   d. Set to desired flow rate
   e. Open Valve V-13, feed valve for MFC5
   f. Set MFC by cylinder to "purge" mode
   g. Open H2S cylinder valve
   h. Open regulator valve
   i. Verify flow by check that reactor pressure has increased

6. Turn RF generator from “stop” to “standby”

7. Start Plasma
   a. Using the secondary monitor, press “Power On” button LabView
   b. Adjust Matching network nobs to minimize reflective energy (must be <5W)
   c. Start pulsing by pressing “Pulse On”
   d. Verify plasma is stable through site glass and Reflected Power is <5W

8. Start Bubbler flow by switching Reactor Bypass 3-way valve from bypass to reactor and start deposition timer
Monitoring Deposition Experiment

1. Recording data for Photo Spectrometer
   a. Press the “Time Acquisition Active Button”
   b. Pressure the “Start Time Aqu.” Button to begin recording (recorded channel is set to 750 nm for Argon)
   c. To save time acquisition data, go to “Time Acquisition” Menu and select “Save Data”
   d. To capture a snapshot of entire spectrum, select “Edit” menu, and Select “Copy Spectral Data” -> “All Spectrometer Channels” to save data or select “Copy Graphical Spectra” to save image.

2. Continue Experiment for desired deposition time. If Reflectance begins to drift to 5W, turn off pulsing and readjust matching network

3. If bubbler pressure starts to increase, make slight adjustment to needle valve to compensate

Ending Deposition and Shutdown

1. Turn off precursor flow by turning Reactor Bypass 3-way valve to bypass position, stop deposition timer

2. Turn off plasma by switching the “Power On” and “Pulse On” to the off positions

3. Turn off Heater by setting Variac to 0 V and turning Variac power off, turn off "OES" and "Site Glass" heating tape

4. Turn off bubbler flow: Close Bubbler Outlet Valve and Bubbler Inlet Valve, open Bubbler Bypass Valve
5. Switch RF Generator to “Stop”, turn off the RF Generator power

6. Turn off H₂S flow
   a. Close H₂S regulator valve
   b. Close H₂S cylinder valve
   c. Wait until MFC by cylinder reads 0 sccm, then Set MFC to "valve closed" mode
   d. Close Valve V-13, turn MFC controller to channel 3 and set flow to 0%, close "H₂S" valve

7. Continue to run Ar through reactor and Bubbler Bypass for at least 30 min to help keep lines purged

8. Turn off Argon
   a. Close Ar cylinder valve
   b. Close Ar MFC2 feed valve, V2, set MFC controller to channel 2 and set to 0%
   c. Close Ar MFC outlet valve, V4 and close manifold valve, V26
   d. Set MFC controller to channel 1 and set to 0%, close MFC1 feed valve, close MFC1 outlet valve, V18, and close 3-way valve

9. Wait until reactor temperature is 100 °C (~1-2 hrs)

10. Put on Hot Gloves and Remove Reactor Heater

11. Close vacuum pump valve and slowly open vacuum break valve

12. When reactor is at atmospheric pressure, put on hot gloves to remove Reactor Lid and remove samples

13. Wipe out any residue in reactor with Kimwipes

14. If running a new experiment, attach new substrates, else place lid back on reactor and pull under vacuum