

# Tuning iron pyrite thin film microstructure by sulfurization of columnar iron precursors

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## ABSTRACT

Iron pyrite is a promising material for photovoltaic power production due to low material extraction and processing costs and high optical absorption. Reliable production of photovoltaic grade iron pyrite thin films has, however, been challenging. One potential fabrication route is the direct conversion of iron-to-iron pyrite by sulfur annealing (sulfurization). Bulk iron thin films are used typically but they can suffer from cracking or delamination. Herein we report the sulfurization of porous, columnar Fe films deposited with Glancing Angle Deposition (GLAD), which allows us to control the inter-column spacing (void-fraction) of the precursor film. We show that the morphology and microstructure of the iron pyrite films are strongly affected by the void-fraction. By precisely tuning the void-fraction of the precursor film at 82° oblique angle incidence deposition we can produce iron pyrite films with increased crystallite sizes > 100 nm with a uniform, crack-free, faceted granular microstructure. Large crystallites may reduce carrier recombination at grain boundaries, which is attractive for photovoltaic devices. Further increasing the void-fraction produces a columnar iron pyrite structure. We also report composition, electrical and optical characterization including a 27 ps lifetime of photocarriers measured with ultrafast optical-pump/THz-probe. Structured, porous precursors offer an alternate route to control microstructure and film stress during fabrication of iron pyrite thin films.

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## 1. Introduction

Iron pyrite is an indirect band gap (0.95 eV) semiconductor material with high optical absorption ( $\alpha_{\text{opt}} > 10^5 \text{ cm}^{-1}$  for  $h\nu > 1.3 \text{ eV}$ ), which results in an absorption length ( $L = 1/\alpha_{\text{opt}}$ ) that is  $10^3$ – $10^4$  times smaller than crystalline silicon [1,2]. The large optical absorption reduces the amount of material required for photovoltaic devices. Combined with the low material extraction costs and processing costs, in part driven by high material abundance, development of iron pyrite photovoltaic cells may contribute to global power production at the terawatt scale [3].

Despite iron pyrite's favorable photovoltaic properties and several decades of experimental and theoretical effort, development of iron pyrite remains incomplete [1,2,4–6]. Some progress towards photovoltaic devices has been made with reports of thin film Schottky cells with Au, Pt, and Nb contacts [1,7], photoelectrochemical cells [4,8–14] and nanocrystal pyrite inorganic-organic hybrid devices [15]. However, power conversion efficiencies

remain low with  $\eta < 0.2\%$  for hybrid cells [15] and  $\eta < 6\%$  for photoelectrochemical cells [10]. A low open-circuit photovoltage ( $V_{\text{OC}}$ ) of < 200 mV in single-crystalline material is one of the main challenges towards improving efficiencies [1,7,10,16,17]. Several mechanisms for the low- $V_{\text{OC}}$  have been proposed and explored in the literature, including bulk non-stoichiometry via vacancies or impurities [1,7,10,18–24]. Fermi level pinning from surface states, [1,19,20,25,26] and phase impurities (such as marcasite or amorphous iron sulfide), [5,16,18,27–29] but a consensus for the cause of low- $V_{\text{OC}}$  has not been reached. Improving device performance will require more complete understanding and control over growth mechanisms, microstructure, surface chemistry, doping and electronic properties, and passivation [1,2].

Thus, development of fabrication methods to meet these challenges has been a major focus. Fabrication techniques including solvothermal synthesis, [30] metal organic chemical vapor deposition, [9,31,32] chemical vapor deposition, [6,33] spray pyrolysis, [34–37] nanoparticle synthesis, [38–41] sputtering, [5,42] sol-gel [43], chemical vapor transport, [4,44,45] and sulfurization of iron and iron oxide precursors films [13,42,46–53] have all been explored but a definitive fabrication method has yet to emerge.

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Sulfurization is attractive for its simplicity and potential low-cost. Typically, bulk Fe precursor films are used, where the microstructure, optical and electrical properties of the iron pyrite are primarily controlled through the sulfurization conditions (e.g., temperature, pressure, duration) [54–60]. Although, some studies have explored the effect of the precursor's structure, such as Fe film thickness and grain size [51,61], the full potential of this technique remains uncultivated.

Conversion of Fe to FeS<sub>2</sub> during sulfurization occurs through an intermediate phase of FeS [54]. Insufficient diffusion through the intermediate FeS layer can lead to incomplete conversion in bulk films several 100 nm thick. However, this issue is mitigated in applications, such as photovoltaics, where only thin layers ~100 nm are required. However, films 100 nm–200 nm thick can suffer from stress-failure, such as buckling or cracking [51,54,62,63]. These problems must be solved to achieve reliable fabrication of iron pyrite films. In addition to thermal stresses at the substrate/film interface, the density difference between iron (7.87 g cm<sup>-3</sup>) and iron pyrite (4.89 g cm<sup>-3</sup>) causes a volume expansion during phase transformation in unconstrained material. Attempts to alleviate stress failures include the addition of adhesion layers [42] and limited attempts to provide room for volume expansion by introducing porosity into the Fe precursor with heated deposition [51].

Here we mature the idea that precursor structure can be used to influence iron pyrite microstructure. We have developed precursors with a columnar morphology and tunable inter-column spacing by using Glancing Angle Deposition (GLAD) [64–66]. GLAD is a physical vapor deposition technique that uses a collimated particle flux and an oblique deposition angle to produce a columnar morphology via geometric self-shadowing. The angle of incidence of the flux, known as the deposition angle ( $\alpha$ ), controls the inter-column spacing (void-fraction) of the

precursor films. A schematic of the deposition geometry and sulfurization process is shown in Fig. 1. Columnar precursors allow sulfur vapor to penetrate the depth of the film to assist sulfurization, [54] and controlling the void-fraction by properly spacing the columns eliminates stress-failures. For the columnar precursors used here, stress-failure is eliminated at deposition angles  $\alpha > 80^\circ$ . Of particular importance, we show that the iron pyrite film microstructure can be modified to achieve uniform films composed of large grains/crystallites that are desirable for photovoltaic application.

We consistently applied a sulfurization recipe derived from an examination of the literature [54–60]. Here we establish that precursor structure, primarily void-fraction, presents an additional mechanism to control iron pyrite microstructure that supplements control through the sulfurization chemistry. Finally, we have characterized the optical and electrical properties, including optical-pump/THz-probe measurements of carrier recombination times, of the films with the largest grains (produced at  $\alpha=82^\circ$ ) to gauge their suitability for device applications and contrast them with other sulfurized iron pyrite thin films.

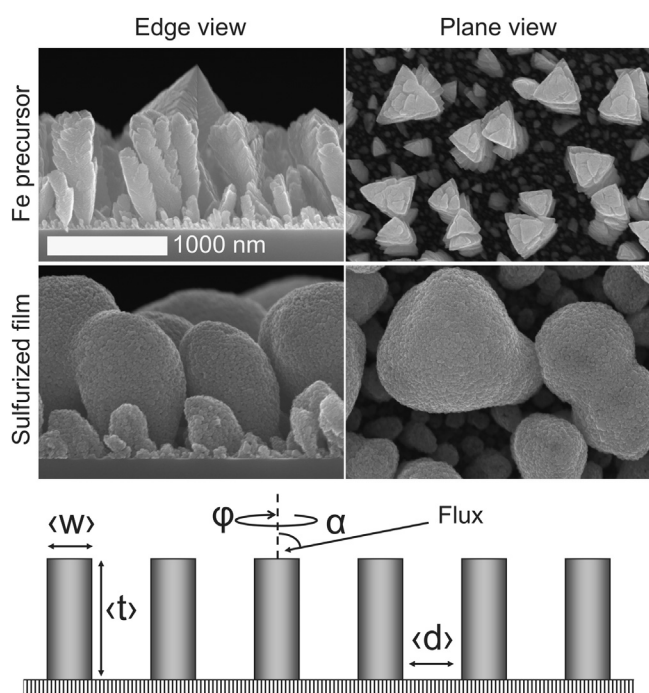
## 2. Experimental section

### 2.1. Iron precursor film deposition

Iron precursor films were deposited with a custom, high-vacuum, electron beam deposition system (Kurt J. Lesker AXXIS) onto unheated Si substrates ({100}, p-type, test-grade, <100  $\Omega$  cm, University Wafer) and fused quartz after reaching a chamber pressure of <0.1 mPa. During deposition this pressure was maintained. Substrates were cleaned by ultra-sonication in de-ionized water, followed by rinses in acetone and isopropanol. The substrates were mounted on a chuck, placed 42 cm from the crucible. Each deposition used source material of elemental iron (cylindrical pieces 3 mm–6 mm in length, 99.95% purity, Kurt J. Lesker) held in a graphite crucible. An electron beam with spot size of 1.5 cm in diameter melted the source material. Nominal flux rate was monitored with a quartz crystal thickness monitor (Maxtex SC-105) and maintained at (0.1 $\pm$ 0.01) nm s<sup>-1</sup> by adjusting the beam current periodically throughout the deposition. Two stepper motors controlled the position of the chuck relative to the collimated flux beam. The vapor flux incidence angle ( $\alpha$ ) was held at a constant value for each deposition, but the azimuth ( $\varphi$ ) was continuously increased (constant rotation). Deposition pitch, the ratio between the nominal flux rate and rotation rate in revolutions per unit time, was held constant at a value of 1 nm for each deposition. A full review of the iron deposition, GLAD technique and the experimental equipment is found elsewhere [64,66,67].

### 2.2. Iron film sulfurization

After deposition, the iron films were sulfurized to produce pyrite (FeS<sub>2</sub>) in sealed quartz ampoules at 450 °C. Quartz ampoules (inner diameter 25 mm) were prepared by cleaning in de-ionized water with sonication, followed by rinses in acetone, isopropanol and ultrapure water. Ampoules are then placed in a glass oven held at 110 °C and left overnight. Sulfur powder was placed in the ampoules (Alfa Aesar, 99.9995%, CAS No. 7704-34-9), so that the partial pressure of S<sub>8(g)</sub> would reach 80 kPa at 450 °C. Typically, 200 mg–250 mg of powder were added to meet this requirement. Si and fused quartz substrates with iron precursor films were also placed in the ampoule, which was then pumped down with a glass diffusion pump for > 1 h before sealing under vacuum. Sealed ampoules were placed in a tube furnace (Lindburg Blue M, one zone) at room temperature and ramped to 450 °C in 45 min, and



**Fig. 1.** Schematic of Fe precursor deposition and example films. Electron micrographs of a Fe precursor deposited at  $\alpha=88^\circ$  and  $t_{\text{Fe}}=936$  nm (1000 nm nominal) and the resulting sulfurized film. A schematic of the deposition geometry is provided to illustrate the deposition angle ( $\alpha$ ) and rotation angle ( $\varphi$ ). Changing the deposition angle ( $\alpha$ ) affects the inter-column spacing ( $d$ ), so that  $d$  tends to increase with  $\alpha$  and thereby increase the void fraction of the film. Column parameters are bracketed in the schematic, to indicate that these parameters are statistical averages over the film.

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