Phase Stability and Stoichiometry in Thin Film Iron Pyrite: Impact on Electronic Transport Properties

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Supporting Information

ABSTRACT: The use of pyrite FeS2 as an earth-abundant, low-cost, nontoxic thin film photovoltaic hinges on improved understanding and control of certain physical and chemical properties. Phase stability, phase purity, stoichiometry, and defects, are central in this respect, as they are frequently implicated in poor solar cell performance. Here, phase-pure polycrystalline pyrite FeS2 films, synthesized by ex situ sulfidation, are subject to systematic reduction by vacuum annealing (to 550 °C) to assess phase stability, stoichiometry evolution, and their impact on transport. Bulk probes reveal the onset of pyrrhotite (Fe1−δS) around 400 °C, rapidly evolving into the majority phase by 425 °C. This is supported by X-ray photoelectron spectroscopy on (001) crystals, revealing surface Fe1−δS formation as low as 160 °C, with rapid growth near 400 °C. The impact on transport is dramatic, with Fe1−δS minority phases leading to a crossover from diffusive transport to hopping (due to conductive Fe1−δS nanoregions in an FeS2 matrix), followed by metallicity when Fe1−δS dominates. Notably, the crossover to hopping leads to an inversion of the sign, and a large decrease in magnitude of the Hall coefficient. By tracking resistivity, magnetotransport, magnetization, and structural/chemical parameters vs annealing, we provide a detailed picture of the evolution in properties with stoichiometry. A strong propensity for S-deficient minority phase formation is found, with no wide window where S vacancies control the FeS2 carrier density. These findings have important implications for FeS2 solar cell development, emphasizing the need for (a) nanoscale chemical homogeneity, and (b) caution in interpreting carrier types and densities.

KEYWORDS: photovoltaic devices, pyrite, thin films, phase stability, stoichiometry, charge transport, doping

1. INTRODUCTION

The pyrite form of FeS2 has long been recognized as a material with high potential as a solar absorber for photovoltaic devices (see ref 1). This is due to pyrite’s exceptional absorption coefficient (>10^5 cm^{-1} above 1.2–1.4 eV), rendering a less than 100 nm thick-film capable of absorbing over 90% of the sun’s light), good mobility (>300 cm^2/V·s in single crystal form), and a suitable minority carrier diffusion length (100–1000 nm). Nevertheless, a significant research effort from the mid 1980s proved unsuccessful in realizing high performance FeS2-based solar cell devices.^1 Short circuit current densities >30 mA cm^{-2} were obtained, along with high quantum efficiency, but with open circuit voltages <0.2 V, limiting power conversion efficiencies to under 3%, even in single-crystal-based photoelectrochemical cells.¹ Such disappointing results led to dwindling interest in pyrite as a solar absorber in the 1990s, particularly in light of the emergence of CdTe and Cu(In,Ga)-Se₂ as thin film photovoltaics.²

This downturn in interest has recently been reversed in light of the realization that FeS₂ may represent a near ideal choice for a photovoltaic material from economic, toxicity, and earth abundance perspectives.³ A number of new thin film⁴–⁶ and nanoparticle/nanowire⁷–¹³ synthesis methods have been developed, and an improved understanding of single crystal properties⁴,¹⁴ defects,⁵,¹⁵–¹⁷ doping,⁵,¹⁶,¹⁸ and surfaces and interfaces¹⁰,¹⁴,¹⁵,¹⁹–²² are being sought. Significantly, a recent publication has reconﬁrmed the poor performance of pyrite, in a variety of solar cell device architectures,²³ underscoring the need to resolve significant fundamental issues with the physical and chemical properties of FeS₂ before progress can be made.

While no single problem underlying the poor photovoltaic performance of pyrite FeS₂ has yet been definitively isolated, a number of potential factors have been identiﬁed. There are, for instance, abundant issues with FeS₂ surfaces and interfaces. Conductive surface layers,¹,⁵,⁶,¹⁰,¹⁴,¹⁵,²⁴ surface inversion layers,¹,⁵,¹⁴,¹⁵,²⁵ surface electronic states,¹,⁵,⁶,¹⁰,¹⁴,¹⁵,²⁴ surface nonstoichiometry, defects, and deep traps,¹,⁵,¹⁰,¹⁵,¹⁶,²⁰–²² and a reduced surface energy gap²⁶ have all been discussed. Doping is another contentious issue in pyrite, where, for example, bulk

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single crystals are almost exclusively n-type\textsuperscript{2,14,27} (perhaps due to S vacancies\textsuperscript{14}), whereas polycrystalline thin films are typically deduced to be p-type\textsuperscript{5,6,10,11,13,28-31}. The fundamental reason(s) for this are not understood, and controlled intentional n- and p-doping of FeS\textsubscript{2} thus remains an outstanding challenge.

Significant in this context is that, of the existing thin film studies, only a small fraction report mobilities sufficiently large that diffusive transport can be safely assumed, and thus Hall measurements simply interpreted. In many other cases, thin film mobilities are so low that interpretation of the Hall coefficient should be explicitly acknowledged as nontrivial. Our recent work with FeS\textsubscript{2} films synthesized by ex situ sulfidation of Fe\textsuperscript{32} emphasized this point, showing that low mobility n-type films can be easily mistaken for p-type, due to the Hall coefficient diminishing and reversing sign, with the onset of hopping transport. This is a well-known phenomenon in disordered semiconductors, a-Si providing the textbook example.\textsuperscript{33-35} In our recent report, the specific situation giving rise to nondiffusive transport was found to be hopping associated with nanoscopic Fe-rich clusters in the FeS\textsubscript{2} matrix, at volume fractions far beneath typical X-ray detection limits.\textsuperscript{32} While these clusters were eradicated at higher processing temperatures,\textsuperscript{32} this nevertheless highlights another issue with pyrite films: the management of nanoscale stoichiometry variations. Also important is the frequently observed low mobility\textsuperscript{1,5,6,11,13,18,32} which seems to be associated with uncontrolled doping at densities up to even $10^{20}$ to $10^{21}$ cm\textsuperscript{-3}\textsuperscript{1,5,6,11,13,18,32} far beyond what can be used in solar cells. Although a number of potential explanations have been advanced, including some ubiquitous uncontrolled dopant\textsuperscript{36,17,18} it is unclear what defect(s) is actually responsible.

The issue of (non)stoichiometry arises frequently in the literature, as will be discussed in detail, these results have numerous implications for future FeS\textsubscript{2}-based solar cell development.

2. RESULTS AND ANALYSIS

As discussed in Section 4 below (Experimental Section), polycrystalline thin film pyrite FeS\textsubscript{2} was synthesized by ex situ sulfidation of Fe. This employed the methods reported in ref 32, essentially 600 °C sulfidation of 33 nm-thick Fe on Al\textsubscript{2}O\textsubscript{3}(0001) substrates, to yield 110 nm-thick polycrystalline pyrite with grain size $\sim$100 nm,\textsuperscript{32} i.e., a "monolayer" of grains. At such high sulfidation temperatures, the films are phase-pure (marcasite-free) pyrite based on laboratory wide-angle X-ray diffraction (WAXRD) and Raman spectroscopy.\textsuperscript{32} Depth-profiled Auger electron spectroscopy measurements reveal a uniform composition profile, albeit with evidence for interdiffusion at the Al\textsubscript{2}O\textsubscript{3}/FeS\textsubscript{2} interface. Energy dispersive spectroscopy (EDS) puts the S/Fe ratio at 1.88 ± 0.10. Importantly, under these synthesis conditions, hopping conduction due to nanoscale Fe-rich clusters is eradicated, with simple activated transport dominating at low temperature (T).\textsuperscript{32} Hall effect measurements unambiguously establish n-type conduction, typical room temperature electron density (n), resistivity (\rho), and mobility (\mu) lying at $10^{20}$ to $10^{21}$ cm\textsuperscript{-3}, 0.1 to 0.01 cm\textsuperscript{2}V\textsuperscript{-1}s\textsuperscript{-1}, and $\sim$0.5 \Omega cm.\textsuperscript{32}

2.1. Bulk Structural/Chemical Characterization. Figure 1(a),(b) presents the WAXRD pattern and Raman spectrum from an as-deposited (unannealed) single-phase polycrystalline pyrite FeS\textsubscript{2} film. In this figure, the lower section of panel (a) shows the expected reflections from cubic pyrite FeS\textsubscript{2} (001) and (monoclinic) pyrrhotite Fe\textsubscript{S}\textsubscript{8} while the lower section of (b) shows the expected Raman peak positions for pyrite FeS\textsubscript{2}.$^{3,10,11,13,40}$ In between the panels, the S/Fe ratio from XPS is listed. Consistent with the above statements, the data from unannealed films suggest phase-pure pyrite FeS\textsubscript{2}.

Figure 1(a,b) also shows the evolution in such bulk characterization data with vacuum annealing temperature (T\textsubscript{A}), through 550 °C. Up to $T_{A} = 350$ °C, the WAXRD and Raman scattering remain essentially unperturbed by annealing, single-phase pyrite FeS\textsubscript{2} being preserved. Consistent with this, the EDS S/Fe ratio is unchanged within experimental uncertainty. A small but distinct change takes place at $T_{A} = 350$ °C.
400 °C, however, where the WAXRD begins to reveal weak reflections associated with polycrystalline pyrrhotite Fe$_{1-\delta}$S, although the S/Fe ratio also decreases at this annealing temperature, to 1.75 ± 0.09. Remarkably, further increasing $T_A$ by only 25 °C, to 425 °C, results in complete suppression of Raman scattering in the probed wavenumber range, a transformation in the WAXRD to a pattern consistent with phase-pure polycrystalline Fe$_{1-\delta}$S, and a sharp drop in the S/Fe ratio to 1.03 ± 0.05. The absence of Raman peaks in pyrrhotite is consistent with prior work, which shows that pyrrhotite is Raman inactive in this window. It is important to note at this stage that the WAXRD results in Figure 1(a) are specifically compared to the Fe$_7$S$_8$ phase of pyrrhotite. As shown in the Supporting Information (SI, see Figure S1), the WAXRD patterns of the various pyrrhotite Fe$_{1-\delta}$S phases are, however, similar, particularly for nonzero $\delta$. While no attempt is made to distinguish among them at this stage, additional data presented below will shed more light on this issue. Further increasing $T_A$ to 450 and 550 °C results in little additional change in WAXRD, nothing in Raman, and only a weak decrease in the S/Fe ratio, which falls to 0.93 ± 0.05 at 550 °C. In short, these bulk structural and chemical probes indicate, as a function of $T_A$ nominally phase-pure pyrite FeS$_2$ up to 350 °C, the onset of a pyrrhotite Fe$_{1-\delta}$S minority phase at 400 °C, followed by a rapid transformation to majority phase pyrrhotite by 425 °C. The evolution in S/Fe is consistent with this, within experimental uncertainty.

2.2. Surface Chemical Characterization. To further probe the evolution in phase stability and stoichiometry with vacuum annealing, in particular to obtain higher sensitivity to the onset of pyrrhotite formation, complementary X-ray photoelectron spectroscopy (XPS) was performed as a function of $T_A$ as described in more detail in Section 4. Given the nature of XPS, which is surface-specific (typically probing no more than the first 2 to 5 unit cells (see the Experimental Section, Section 4, below for more details), and sensitive to crystalline orientation, this aspect of the characterization was performed not on polycrystalline films, but on single crystal FeS$_2$. As described in more detail in Section 4 below, and following an adaptation of a method previously used for high quality CoS$_2$, a variant of chemical vapor transport (CVT) was employed to grow the crystals. This resulted in stoichiometric, phase-pure, single crystal pyrite FeS$_2$ specimens, as verified by WAXRD, Raman, EDS, and X-ray diffraction with a 2D area detector. A summary of the results is provided in the SI (see Figures S2 and S3). The (001) surfaces were identified by crystal habit, verified by X-ray diffraction with a 2D detector, and used for the XPS measurements. In terms of surface preparation, Ar ion sputtering and annealing procedures were found to alter the surface stoichiometry and lower the pyrite FeS$_2$(001) surface stability (as previously reported), and thus were avoided. The measurements were performed at a photon energy of 1486.6 eV. This is relatively high in comparison to some prior work, and thus less sensitive to the extreme surface region.

The S 2p core level formed the focus of these XPS studies, as this spectral region provides information on the nature of the bonding with Fe, the nominal Fe valence, and the surface stoichiometry. As shown in Figure 2(a), unannealed pyrite FeS$_2$(001) single crystal surfaces show the S 2p$_{3/2}$/2p$_{1/2}$ doublet around 162.8 ± 0.2 eV in binding energy, with an intensity ratio near 0.5. For reference, prior studies report the S 2p$_{3/2}$ core level binding energy as 162.6, 162.9, and 163.1 eV in good agreement with the results shown here. With increasing $T_A$ up to 380 °C, this S 2p doublet gradually shifts to lower binding energies, following a clear and abrupt transformation between 380 and 410 °C, where a new S 2p doublet at 162.6 ± 0.3 and 161.4 ± 0.2 eV emerges. The spectra then continue to gradually evolve through $T_A = 530$ °C, resulting by 600 °C in a simple doublet shifted by ~1.3 eV from the FeS$_2$ starting point (unannealed data). Reference to prior literature confirms that the spectrum at 600 °C is in fact quantitatively similar to prior work on pyrrhotite Fe$_{1-\delta}$S and associated by Andersson et al. and Herbert et al. with S vacancies in FeS$_2$. Between ambient and 600 °C the spectra were thus fit to a four peak model, describing the S 2p$_{3/2}$ and 2p$_{1/2}$ peaks for both FeS$_2$ and Fe$_{1-\delta}$S. This process is illustrated for the representative case of $T_A = 450$ °C in Figure 2(a), showing the four individual peaks in addition to the background (see figure caption for details). These intensities were then used to extract the molar phase fractions of FeS$_2$ and Fe$_{1-\delta}$S, resulting in the $T_A$ dependence shown in Figure 2(b). Note that the use of S 2p core level spectra enables this analysis with no need for corrections due to the energy-dependent electron analyzer transmission function, photoemission cross sections, or mean-free-paths.

As expected from inspection of Figure 2(a), minor amounts of Fe$_{1-\delta}$S begin to form on the pyrite surface after vacuum annealing at temperatures as low as 160 °C, but with a remarkably rapid increase between 380 and 410 °C. Above this temperature, the pyrrhotite molar fraction steadily increases, reaching about 0.9 by 600 °C. While the important distinctions between surface and bulk sensitivity, and (001) vs. random
orientation, must be kept in mind when comparing Figures 1 and 2, the results are broadly consistent. Minor pyrrhotite formation, likely limited to the surface, occurs at as low as 160 °C in vacuum, followed by far faster conversion to pyrrhotite around 380 °C. In polycrystalline films, the latter is likely initiated at the surface and in the grain boundary regions. By 410 °C, however, the transformation from pyrite FeS₂ to pyrrhotite Fe₁−δS is substantially complete, and Fe₁−δS becomes the majority phase. Vacuum annealing at still higher temperatures results in near phase-pure Fe₁−δS.

### 2.3. Electronic (and Magnetic) Properties

In order to probe the impact on electronic transport properties of the phase and stoichiometry evolution with vacuum annealing captured in Figures 1 and 2, wide T range ρ(T) measurements were made at various T_A. As shown in Figure 3(a), the unannealed polycrystalline pyrite FeS₂ films have ρ ≥ 0.5 Ωcm at 300 K, monotonically increasing to >10³ Ωcm on cooling to liquid helium temperatures. Vacuum annealing at T_A up to 400 °C results in what appear to be only relatively small changes in ρ(T), clear semiconducting-like (dρ/dT ≪ 0) behavior being preserved. This is consistent with retention of a pyrite FeS₂ majority phase up to 400 °C, as seen in Figure 1. Between 400 and 425 °C, however, where the structural/
chemical data (e.g., Figure 1) reveal a sharp transition from a pyrite to pyrrhotite majority phase, the $p(T)$ behavior also abruptly alters. The low $T$ resistivity in fact falls by over 6 orders of magnitude between $T_A = 400$ and 425 °C, the strongly semiconducting behavior at $T_A \leq 400$ °C transitioning to a regime of small negative $\delta p/\delta T$ and mΩcm resistivities at $T_A = 425$ °C. This is consistent with the established electronic properties of pyrrhotite Fe$_{1-x}$S, which is known to be a good conductor; room temperature $\rho$ is in the 0.1–1 mΩcm range in naturally occurring single crystals.37,46

To probe this transformation more deeply, particularly around $T_A \approx 400$ °C where pyrrhotite begins to form as a bulk minority phase, Zabrodskii plots47 can be used. These are $\ln W$ vs $\ln T$ plots, where the quantity $W$, termed the reduced activation energy, is defined as $W = -\delta p/\delta T$. On such plots $\ln W$ decreasing as $\ln T$ is lowered is characteristic of conduction on the metallic side of the metal–insulator transition (MIT), whereas $\ln W$ increasing as $\ln T$ is lowered is indicative of conduction on the insulating side of the MIT. Moreover, if the resistivity on the insulating side of the MIT is of the form $\rho = \rho_0 \exp (T_{0}/T)^{m}$, where $\rho_0$ is the $T$ → 0 value of the resistivity and $T_0$ is some characteristic temperature, a $\ln W$ vs $\ln T$ plot linearizes this form, resulting in a straight line of slope $= m$.47 This provides a quantitative, unbiased means to extract $m$, which is indicative of the active transport mechanism. As discussed in our prior work,32 and in more detail elsewhere,48,49 $m = 1$ corresponds to simple activated behavior ($\rho = \rho_0 \exp (T_{0}/T)$), as for conventional thermal activation from some dopant level. Values of $m$ of 1/4 or 1/2 on the other hand (i.e., $\rho = \rho_0 \exp (T_{0}/T)^{1/4}$ or $\rho = \rho_0 \exp (T_{0}/T)^{1/2}$, respectively), indicate variable-range hopping (VRH) of either Mott type (constant density-of-states around the Fermi level), or Efros–Shklovskii type (where electron–electron interactions open a soft-gap at the Fermi energy).58

As discussed in ref 32, in an inhomogeneous semiconductor, an alternative explanation for $m = 1/2$ is possible, associated with conductive clusters in a more insulating matrix. Specifically, if these clusters are sufficiently small (nanoscopic), the Coulombic energy penalty associated with charging a cluster with a single hopping electron ($e^2/4\pi\epsilon d$, where $\epsilon$ is the electronic charge, $d$ is the dielectric constant, and $d$ is the cluster diameter) becomes significant, resulting in “granular metallic conduction”. Early modeling of this situation by Abeles, Sheng, and co-workers50,51 ascribed the conduction to hopping between conductive clusters, which they argued results in $\ln W = \ln \rho_0 \exp (T_{0}/T)^{1/2}$. Their derivation, however, relied on a specific assumption regarding the ratio of $d$ to the intercluster separation.50,51 This assumption was later criticized by a number of authors, on both experimental and theoretical grounds.52–54

Zhang and Shklovskii thus advanced an alternative picture where doping in the insulating matrix leads to random charging of the conductive clusters, and finite density-of-states at the Fermi level.53 This density-of-states is soft- rather than hard-gapped, recovering Efros–Shklovskii $\rho = \rho_0 \exp (T_{0}/T)^{1/2}$ behavior.53 For the current paper, the essential point is that detection of $m = 1/2$ can indicate conventional Efros–Shklovskii VRH in a homogeneous semiconductor, but can also result from conductive nanoregions in a more insulating matrix. The latter was in fact directly implicated in our prior work on ex situ sulfidized FeS$_2$ films, where sulfidation temperatures below the 600 °C used here resulted in nanoscopic unreacted Fe-rich clusters.32

To directly determine $m$ in the current case, where the electronic transport is controlled by the vacuum annealing temperature, $T_A$, Figure 3(b) plots $\ln W$ vs $\ln T$ for the films shown in Figure 3(a). As expected,32 the unannealed FeS$_2$ film has $m = 0.84$ at low $T$, the proximity to unity indicating close to simple activated transport. (As discussed in full in ref 32, strict adherence to simple activated behavior over a broad $T$ range is not seen in these FeS$_2$ films; further mitigation of the high doping density and low mobility will be needed to obtain truly diffusive transport). As $T_A$ is increased to 250 °C, this behavior is largely unchanged, although $m$ falls slightly to 0.74.

At 350 and 400 °C, the situation is remarkably different, which is not obvious from direct inspection of Figure 3(a). At these $T_A$ values, not only does $\ln W$ become linear in $\ln T$ over an exceptionally wide $T$ range (from ambient to liquid helium temperatures), but $m$ also collapses to a value close to 1/2. The form $\rho = \rho_0 \exp (T_{0}/T)^{1/2}$ is thus robustly adhered to, specifically in the $T_A$ region where structural and chemical characterization reveal the onset of the bulk pyrrhotite minority phase. In light of (a) our prior work demonstrating how readily conductive nanoclusters can induce such hopping conduction in pyrrhotite thin films,37 (b) the simultaneity of the observation of $\rho = \rho_0 \exp (T_{0}/T)^{1/2}$ with the onset of a pyrrhotite bulk minority phase, and (c) the known conductive nature of pyrrhotite,37,46 we conclude that hopping associated with conductive pyrrhotite nanoregions in a more insulating matrix of FeS$_2$ is active. Careful annealing time studies at $T_A = 350$ °C corroborate this picture. As shown in SI Figure S4, for example, anneals for 1, 24, and 72 h reveal the monotonic growth of a pyrrhotite37,46 we conclude that hopping associated with conductive pyrrhotite nanoregions in a more insulating matrix of FeS$_2$ is active. Careful annealing time studies at $T_A = 350$ °C corroborate this picture. As shown in SI Figure S4, for example, anneals for 1, 24, and 72 h reveal the monotonic growth of a pyrrhotite minority phase. This consistently results in electronic transport with $m \approx 1/2$, extracted values at these annealing times being 0.49, 0.48, and 0.49, with impressively close adherence to $\rho = \rho_0 \exp (T_{0}/T)^{1/2}$, over the entire measured $T$ range (SI Figure S5). At 350 and 400 °C, five separate samples (in Figure 3 and SI Figure S4) thus result in $m$ values of 0.49, 0.61, 0.49, 0.48, and 0.49, which we take as strong evidence of $m = 1/2$. This conclusion comes from $\rho(T)$ data sets with >2000 points, spanning more than an order of magnitude in $T$ (300 to <20 K) and four decades of resistivity.

It is important to emphasize that comparison of Figures 1 and 2 implies, unsurprisingly, that the reduction of FeS$_2$ initiates at the surface, and it is thus logical that the significant volume fraction of Fe$_{1-x}$S that emerges around $T_A \approx 350–400$ °C does so in localized regions at the surfaces and grain boundaries of the FeS$_2$ crystallites. This overall picture is clearly related to the hopping induced by nanoscale unreacted Fe clusters due to inadequate sulfidation in ref 32, but in this case is due to nanoscopic Fe$_{1-x}$S clusters forming upon reduction of FeS$_2$ likely at the grain interfaces/surface. Even further evidence for these conclusions will be provided below, from magnetic and magnetotransport measurements.

As a final comment on the data shown in Figure 3(b), note that, as expected from Figure 3(a), the Zabrodskii plots at $T_A \geq 425$ °C show $\ln W$ decreasing on cooling (Figure 3(b)), indicative of metallic transport. Consistent with this, plots of low temperature conductivity vs $T$ suggest finite conductivity as $T \rightarrow 0$ for 425 and 450 °C, implying metallic behavior; at 550 °C the behavior is close to the metal–insulator transition. This overall behavior reflects the emergence of the conductive Fe$_{1-x}$S pyrrhotite majority phase (Figures 1 and 2) with increasing $T_A$. In the SI (Figure S6), we in fact provide an example of a film that was vacuum annealed under slightly different conditions, resulting in a sufficiently conductive
pyrrhotite majority phase that positive $d\rho/dT$ is maintained over a wide $T$ range. This is consistent with the metallic character of pyrrhotite.\textsuperscript{37,46}

Further insight is obtained from measurements of the Hall effect, which are shown in Figure 4(a) for an unannealed sample as well as representative $T_A$ values of 250, 350, and 550 °C. The data are presented as Hall resistivity, $\rho_{xy}$ (zero field background subtracted) vs applied magnetic field, $H$, at 290 K. Again consistent with our prior work\textsuperscript{32}, the unannealed FeS$_2$ film exhibits a robust, field-linear Hall signal, the slope of $\rho_{xy}(H)$ being electron-like (negative). Given that we have clearly demonstrated that hopping transport does not occur in this $T$ range in such unannealed samples, this can be definitively ascribed to $n$-type conduction. Following the simplest analysis results in $n = 5.7 \times 10^{20}$ cm$^{-3}$, and $\mu = 0.03$ cm$^2$V$^{-1}$s$^{-1}$ at 290 K. The dopant responsible for the $n$-type conduction in our case, and the heavy doping level (which is common in pyrite films) remains to be clarified, and is a major open issue in the field. At $T_A = 250$ °C, the Hall coefficient ($R_H = \rho_{xy}/\mu B$) is significantly decreased in magnitude, however, and, at 350 °C, it in fact changes sign to hole-like. This small positive $R_H$ is then maintained as $T_A$ is increased to 550 °C. Vitaly, the sign reversal in $R_H$ is coincident with the conversion to a pyrrhotite majority phase and the associated metal–insulator transition ($T_A \approx 425$ °C, Figures 1 and 3), but with the first onset of a bulk pyrrhotite minority phase and the associated crossover to hopping ($T_A \approx 350$ °C, Figure 3(b)). This is therefore clearly the sign-reversal (and suppression) of $R_H$ due to the onset of hopping conduction,\textsuperscript{32,35} as discussed in Section 1; it occurs well before the coalescence and percolation of pyrrhotite into a majority phase. That $R_H$ remains positive and relatively small as $T_A$ is further increased, and pyrrhotite begins to dominate, consistent with the established high $p$-type carrier densities at room temperature in pyrrhotite single crystals.\textsuperscript{46} In our case, we obtain $p = 6.5 \times 10^{21}$ cm$^{-3}$ and $\mu = 0.25$ cm$^2$V$^{-1}$s$^{-1}$ when pyrrhotite dominates, again using the simplest model that assumes one dominant carrier type. The crossover to hopping transport at $T_A \approx 350$ °C (Figure 3(b)) that is so clearly reflected in the Hall effect (Figure 4(a)) is also evident from magnetoresistance (MR) data. Specifically, as shown in Figure 4(b), the MR ([($\rho(H) - \rho(0))/\rho(0)$] × 100%) in unannealed and 250 °C films is positive and approximately parabolic at a cryogenic temperature of 20 K, amounting to ~1%. These data are taken with $H$ perpendicular to the film plane (and therefore the current), and the positive quadratic MR thus adheres well to expectations for diffusive/band transport in a nonmagnetic semiconductor. At $T_A = 350$ °C, however, this simple positive MR is replaced with more complex nonmonotonic behavior, a negative contribution emerging at the highest $H$. This is exactly as seen with decreasing sulfidation temperature in our prior work\textsuperscript{32} and interpreted in terms of magnetism in the conductive nano-clusters (Fe-rich in that case) that induce hopping conduction. In the current case pyrrhotite Fe$_{1-x}$S is also magnetically ordered,\textsuperscript{37} and thus this explanation remains relevant.

To further probe the possibility of nontrivial magnetism due to the reduction of FeS$_2$, magnetization hysteresis loops ($M(H)$) were recorded at 200 K at various important $T_A$ values, as shown in Figure 4(c). The diverse magnetic behaviors of the various constituents of the Fe–S phase diagram render such measurements sensitive to the phases present, potentially even more so than the data of Figure 1. Specifically, FeS$_2$ is a zero-spin diamagnet\textsuperscript{32,37} and Fe is obviously a long-range ordered ferromagnet with a high Curie temperature, while the magnetic ground states of the intermediate Fe sulﬁdes are nontrivial. Briefly, troilite FeS is an antiferromagnet with a Néel temperature near 590 K,\textsuperscript{35} whereas pyrrhotite Fe$_{1-x}$S is ferrimagnetic,\textsuperscript{37} with magnetization and ordering temperature strongly dependent on $\delta$.\textsuperscript{35} At the Fe$_{x}$S$_{1-x}$ composition, for

![Figure 4](image-url)
instance, a ferrimagnet with an ordering temperature of 580 K has been reported.\textsuperscript{37} Examining the 200 K data in Figure 4(c), we first find in the unannealed phase-pure FeS\textsubscript{2} film negligible magnetization, consistent with the expectation of diamagnetic response from phase-pure pyrite. As $T_A$ is increased the situation is unchanged (data not shown) until 425 °C. At this point, clear saturation magnetization turns on (at about 0.025 $\mu_B$/Fe), with a ferromagnetic-like $M(H)$, increasing to 0.1 $\mu_B$/Fe at $T_A = 450$ °C. This is consistent with Figures 1 and 2, the magnetization being ascribed to the growing volume fraction of ferrimagnetic pyrrhotite. This is a strong indication that the specific Fe$_{1-\delta}$S phase in this $T_A$ region is close to Fe$_{8}$S$_{14}$, a suspicion that is backed up by the measurement of a magnetic ordering temperature well above 300 K (SI Figure S7), consistent with the known properties of this phase. Interestingly, as $T_A$ is increased further, to 550 °C, the magnetization drops again, falling to negligible levels. One possible interpretation (consistent with the S/Fe ratio from EDS (Figure 1)) is that the $\delta$ in Fe$_{1-\delta}$S decreases with $T_A$, reaching $\delta \approx 0$ at 550 °C, i.e., a transformation from ferrimagnetic pyrrhotite Fe$_{7}$S$_{8}$ toward antiferromagnetic trolite FeS.$^{55}$

3. DISCUSSION AND CONCLUSIONS

The left panel of Figure 5 provides a summary of the main findings of this work. Specifically, Figure 5(a)–(f) shows the $T_A$ dependence of the key quantities extracted from the structural/chemical characterization and transport/magnetic measurements, depicting unanneled films simply at $T_A = 0$. The panels (a) through (f) plot, respectively, the EDS S/Fe ratio (with the dominant chemical phase labeled above the panel), the resistivity ($\rho$) at 20 and 300 K, the limiting low $T$ value of the exponent $m$ in $\rho = \rho_0 \exp \left( T_0/T \right)^m$, the magnitude of the Hall coefficient, $R_H$ (with the sign indicated), the 90 kOe magnetoresistance (MR) value, and the saturation magnetization ($M_S$) at 200 K. The crossover in primary phase between pyrite FeS$_{2}$ and pyrrhotite Fe$_{1-\delta}$S between 400 and 425 °C is marked by the vertical orange dotted line.

While the overall transformation in majority phase at around 400 °C is abundantly clear from Figure 5(a), a number of other features warrant further discussion and reiteration. The first is the diffusive to hopping transport crossover that takes place prior to the pyrite to pyrrhotite majority phase transformation, i.e., to the left of the dashed vertical line. This crossover is most clearly reflected in the decrease in $m$ in Figure 5(c) to $m \approx 0.5$, but is also reflected more subtly in the resistivity data shown in Figure 2(b), as the upturn in the low $T$ value. This is of course a consequence of the changes in $\rho_0$ and $T_0$ and $m$ that take place in $\rho = \rho_0 \exp \left( T_0/T \right)^m$ at the crossover point, i.e., the entry to the hopping regime associated with the pyrrhotite nanocluster minority phase. As already mentioned, the evidence for $m = 1/2$ in the 350–400 °C range is strong, the increase at lower $T_A$ being due to the crossover toward $m = 1$. As discussed in Section 2.3, this hopping transport also leads to suppression of the magnitude of $R_H$ in addition to a sign change from negative to positive (Figure 5(d)). We reiterate that this reflects the unambiguously n-type conduction in the unannealed films, crossing over at $T_A \approx 350$ °C to a regime where the sign of $R_H$ is inverted, not due to some unexplained $n$ to $p$ crossover, but to the failure of the Hall effect to accurately reflect the true sign of the charge carriers (Section 1). The rise in $R_H$ on further increasing $T_A$ and crossing the vertical dashed line in Figure 5(d) is then due to the onset of the majority pyrrhotite phase, a hole conductor.$^{37,46}$ The MR data of Figure 5(c) are consistent, the small positive MR expected from a nonmagnetic semiconductor such as FeS$_{2}$ in the diffusive transport regime being replaced with more complex (Figure 4(b)) MR in the hopping regime, even dipping to net negative values in the crossover region (Figure 5(e)). This is ascribed to magnetism in the pyrrhotite nanoclusters that induce the hopping transport. Finally, as shown in Figure 5(f), the magnetic behavior from Figure 4(c) can be summarized by the $T_A$ dependence of the 200 K $M_S$. This reveals the rapid increase in $M_S$ associated with the ferrimagnetic Fe$_{8}$S$_{8}$ pyrrhotite phase, followed by the

![Figure 5](https://example.com/figure5.png)

**Figure 5.** Annealing temperature ($T_A$) dependence of (a) the S to Fe ratio from energy dispersive spectroscopy, (b) the 20 and 300 K resistivity, $\rho$, (c) $m$, the exponent in $\rho = \rho_0 \exp \left( T_0/T \right)^m$, (d) the magnitude of the 290 K Hall coefficient, $R_H$, (e) the 20 K magnetoresistance at 90 kOe, and (f) the 200 K saturation magnetization, $M_S$. Note that $T_A = 0$ indicates “unannealed”. In panel (c), the horizontal dashed lines mark $m = 0.5$ and 1. In panel (d), the $\pm$ symbols indicate the sign of the Hall coefficient, and the arrow represents an upper bound. The vertical orange line indicates the point at which the majority phase converts from pyrite FeS$_{2}$ to pyrrhotite Fe$_{1-\delta}$S. The same parameters, $\rho$, $m$, $R_H$, MR(90 kOe), and $M_S$, are plotted as a function of the S/Fe ratio in panels (g), (h), (i), (j), and (k).
4. EXPERIMENTAL SECTION

Polycrystalline FeS₂ films were fabricated by ex situ sulfidation. In the first step, 33 nm thick (from grazing incidence X-ray reflectivity) Fe films were deposited on large (approximately 50 × 4 mm²) chemically cleaned Al₂O₃(0001) substrates via DC magnetron sputtering (base pressure typically <1 × 10⁻⁸ Torr) from an Fe target (Kurt J. Lesker, 99.9% purity). An Ar pressure of 2.3 mTorr and a substrate temperature of 300 °C were used, resulting in a deposition rate of 0.08 nm/s and (110) out-of-plane texture. The Fe films were then placed in an evacuated (10⁻⁶ Torr) and sealed quartz ampule (8 cm³) with 1.0 ± 0.1 mg of S (CERAC, 99.999% purity) and sulfidized. Heating took place at 6.5 °C/min, followed by isothermal sulfidation at 600 °C for 8 h (estimated S pressure 35 Torr) followed by furnace cooling. Care was taken to avoid S condensation on the film during cooling.

As-made FeS₂ films were then fractured into multiple pieces (approximately 4 × 4 mm²) for WAXRD, SEM/EDS, Raman spectroscopy, electronic transport, and magnetometry. Vacuum annealing of these films was performed at a single temperature (T₀), between 250 and 550 °C, for 1 h, in a chamber with a base pressure ~1 × 10⁻⁸ Torr. WAXRD data were then collected with a Bruker-AXS PLATFORM X-ray diffractometer equipped with a Cu source, a graphite monochromator (Kα pass-through filter), a 0.8 mm incident beam point collimator, and a 2D Hi-Star area detector. Microstructure and composition were examined using a JEOL 6500F field emission SEM with a Thermo-Noran Vantage EDS system, and Raman data were collected in the backscattering geometry using a WiTec alpha300R confocal microscope equipped with a UHTS 300 spectrometer and a DV401 CCD detector. Temperature- and field-dependent transport measurements (5—300 K) were made in a Janis cryostat and/or a Quantum Design Physical Property Measurement System (PPMS), both equipped with 9 kOe superconducting magnets. Soldered indium contacts in a van der Pauw configuration were employed, using AC (13.7 Hz) and DC excitation, depending on the magnitude of the resistance. Extensive checks for ohmicity, excessive contact resistance, and self-heating were made. Hall measurements were done AC (with a resistance bridge), paying particular attention to temperature stability. Magnetometry was done in a Quantum Design Superconducting Quantum Interference Device (SQUID) magnetometer from 5 to 300 K in fields up to 70 kOe.

Single crystals of FeS₂ were grown via a chemical vapor transport (CVT) method (see refs 15 and 41, and references therein), in which FeS₂ (Alfa Aesar, 99.9% purity) and S (CERAC, 99.999% purity) were employed as source materials, with FeBr₂ (Sigma-Aldrich, 99.999% purity) as a transport agent. Briefly, 2.2 g of FeS₂ powder, 100 mg of FeBr₂ powder, and 580 mg of S powder were loaded into an evacuated (10⁻⁶ Torr) and sealed quartz ampule (52 cm³) in a two-zone tube furnace. The source materials were loaded into the “source zone”, crystals nucleating in the “growth zone”. The temperatures of the source and growth zones were first (for the initial 72 h) set at 700 and 730 °C, respectively, i.e., with the growth zone hotter than the source zone. This is an approach frequently used in CVT, designed to establish an equilibrium vapor state, and to help “catch” the growth zone of excess potential nucleation sites. CVT growth was then...
initiated by reversing the temperature gradient, setting the source and growth zones to 670 and 590 °C, respectively. This was maintained for 3 weeks typically, resulting in pyrite single crystals with up to 5 mm wide facets. Phase purity was established with X-ray powder diffraction (with a Bruker-AXS D5005 Diffractometer on powdered crystals) and Raman spectroscopy. Chemical composition was confirmed using EDS, while single crystallinity was confirmed by X-ray diffraction with a 2D area detector (on the same Bruker system described above). Characterization results are provided in SI Figures S2 and S3.

Core level XPS was done on several FeS2 single crystals in a PHI Versa Probe II system with a monochromatic Al Kα anode X-ray source (hν = 1486.6 eV) and a hemispherical analyzer. Measurements were carried out in ultrahigh vacuum (UHV, around 8 × 10−10 Torr), annealing being done with a temperature cycle that involved warm-up in ~10 min, ~10 min of equilibration, and cool-down in ~10 min. As discussed in Section 2.2, standard Ar ion sputter/anneal procedures were avoided. All spectra were recorded using the PHI software package SmartSoft—XPS v2.0 and processed using PHI Multipack v9.0 and/or CASA XPS v2.3.14. The positions of the S 2p1/2 and 2p3/2 peaks for FeS2, FeS3−δ, and FeS2−δ were identified based on prior literature.21,22,44,45 The 2p1/2 and 2p3/2 states have an energy spacing of about 1.1 eV, and an intensity ratio of 2.0–2.4. Peaks were fitted using GL line shapes (a widely used hybrid of Gaussian and Lorentzian),57 with Shirley background subtraction.58,59 Up to 50 scans were accumulated and averaged to improve the signal-to-noise ratio for each spectrum. The samples were also examined at 5–6 locations, establishing reproducibility. Note that under the conditions used here, XPS is expected to probe no more than 2–5 unit cells. This is supported by angle-resolved data, which indicate that more than 50% of the signal comes from the top 1.5 nm.

■ ASSOCIATED CONTENT

 Supporting Information
Additional structural, chemical, electronic, and magnetometry measurement results. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b03422.

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Notes
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