Crossover From Nanoscopic Intergranular Hopping to Conventional Charge Transport in Pyrite Thin Films

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ABSTRACT Pyrite FeS₂ is receiving a resurgence of interest as a uniquely attractive thin film solar absorber based on abundant, low-cost, nontoxic elements. Here we address, via ex situ sulfidation synthesis, the long-standing problem of understanding conduction and doping in FeS₂ films, an elusive prerequisite to successful solar cells. We find that an abrupt improvement in crystallinity at intermediate sulfidation temperatures is accompanied by unanticipated crossovers from intergranular hopping to conventional transport, and, remarkably, from hole-like to electron-like Hall coefficients. The hopping is found to occur between a small volume fraction of conductive nanoscopic sulfur-deficient grain cores (beneath our X-ray diffraction detection limits), embedded in nominally stoichiometric FeS₂. In addition to placing constraints on the conditions under which useful properties can be obtained from FeS₂ synthesized in diffusion-limited situations, these results also emphasize that FeS₂ films are not universally p-type. Indeed, with no knowledge of the active transport mechanism we demonstrate that the Hall coefficient alone is insufficient to determine the sign of the carriers. These results elucidate the possible transport mechanisms in thin film FeS₂ in addition to their influence on the deduced carrier type, an enabling advancement with respect to understanding and controlling doping in pyrite films.

KEYWORDS: iron pyrite · photovoltaics · hopping conduction · Hall effect · doping

The development of photovoltaic (PV) materials suitable for large-scale deployment of solar-to-electric power conversion devices is one of the biggest challenges of our time. Ideal materials would not only display high absorption in the visible, enabling use of thin film solar cells to minimize materials costs, but would also comprise earth-abundant, low-cost, nontoxic elements, amenable to large-scale production. While the materials dominating the current PV market (Si, CdTe, and CuInGaSe₂) each offer unique advantages, none are able to satisfy all of these requirements. For example, the indirect band gap of crystalline Si leads to relatively poor solar absorption and thus to the need for high thickness (and materials costs), while CdTe and CuInGaSe₂ suffer from concerns over either low earth abundance of some of their constituents (e.g., In, Te), toxicity (e.g., Cd), or both.

Pyrite structure FeS₂ on the other hand, has long been acknowledged as a material with outstanding potential to satisfy these criteria. The pyrite band gap lies in a useful region (~0.95 eV) and the absorption coefficient exceeds a remarkable 10⁴ cm⁻¹ above 1 eV, rendering a thickness of <100 nm sufficient to absorb >90% of sunlight. This can be compared to >200 μm for Si. It is thus unsurprising that, from the mid 1980s, significant research focused on the development of FeS₂-based PV. Having yielded cell efficiencies <3% and open circuit voltages of only ~0.1 V, this effort was not entirely successful. Although no single origin for these disappointing results emerged, a number of serious issues were identified. Prominent among these is that thin film FeS₂ conduction and doping mechanisms are poorly understood. In particular, crystals are typically n-type, while, in the majority of cases, thin films appear to exhibit p-type conduction. This is not understood, and indeed the primary electrically active defects expected in FeS₂ remain a matter of debate.

One important consequence of this inability to understand doping in FeS₂ films is that the work evolved away from

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potentially simpler p–n homojunction or p–i–n cells, instead favoring photoelectrochemical and metal/FeS2 Schottky-type devices.2 The failure of such devices to yield large open circuit voltages or efficiencies has been interpreted many ways, the existence of uncontrolled surface states and defects being one widely cited example.2–4 Given these difficulties, and the emergence of materials such as CdTe and CuInGaSe2, interest in FeS2 films for PV waned.

Very recently, the outstanding potential of FeS2 as a solar absorber, in tandem with the minimal toxicity and low costs of Fe and S, has stimulated renewed interest. New synthesis routes are being explored,3,4,9 substantial efforts are being made to understand defects/doping3,4,7,8 and surfaces/interfaces4,9,13 and properties are being revisited.3,4,9 It is in this context that we have performed a detailed study of electronic conduction in thoroughly characterized FeS2 thin films synthesized via one of the simplest techniques: ex situ sulfidation of Fe.14–20 The results reveal a significant surprise. Specifically, as the sulfidation temperatures are increased above 400–450 °C we observe a crossover in the conduction mechanism, from hopping to a more conventional band transport-type mechanism. Through detailed analysis of the transport parameters, characterization of the Fe spin-state, and simple calculations on S diffusion, we demonstrate that this hopping occurs via conductive S-deficient nanoscopic grain cores (at volume fractions beneath typical lab X-ray detection limits), embedded in nominally stoichiometric FeS2. As the sulfidation temperature is increased, and diffusion improves, this gives way to more conventional transport. The implications in terms of expectations for device performance from films synthesized under diffusion-limited conditions are quite clear. Moreover, the conduction crossover is found to be accompanied by an abrupt sign reversal of the Hall coefficient, from hole-like (in the hopping regime) to electron-like. In addition to emphasizing the need to fully understand transport mechanisms in order to reliably interpret the sign of the Hall coefficient, our findings also highlight that FeS2 thin films are not universally p-type.

RESULTS AND DISCUSSION

As described in more detail in the Methods section and in Supporting Information (SI), FeS2 films were prepared by ex situ sulfidation of 33 nm thick Fe films on Al2O3(0001) at sulfidation temperatures, Tn, between 100 and 800 °C. Wide-angle X-ray diffraction (WAXRD) data as a function of Tn are shown in Figure 1. As discussed in SI, these data were obtained by integrating 2D area scans, and are normalized to thickness, and intensity of the Al2O3 (0006) substrate peak. Expected powder patterns for pyrite FeS2, marcasite FeS2 (the well-known FeS2 polymorph), and metallic Fe are shown for comparison. Below 200 °C, although energy dispersive spectroscopy (EDS) detects ∼5 atom % S, only the reflections from metallic Fe are observed, indicating that crystalline Fe–S compounds do not yet form in detectable quantities. This changes radically at Tn ≥ 200 °C (in reasonable agreement with prior work),15,18 where multiple peaks indexable to pyrite FeS2 are observed, growing in intensity with Tn, particularly above 400 °C. Only at Tn = 800 °C is any evidence for a minor marcasite impurity phase found (peaks labeled with an asterisk). We thus conclude, with the usual caveats regarding WAXRD detection limits, that single-phase,21 nominally untexured, pyrite FeS2 is obtained over a wide range of Tn from 200 to 700 °C. Scanning electron microscopy (SEM) images of films sulfidized between 200 and 700 °C are shown in Figure 2, in both plan (top panel) and tilt (bottom panel) views. At Tn ≤ 400 °C we find a dense array of quite monodisperse ∼60 nm diameter grains, forming relatively smooth polycrystalline films.22 Above 400 °C however, rapid grain growth occurs, accompanied by an increase in surface roughness and faceting as the grain size approaches the thickness. Somewhat similar behavior has been observed in prior work on ex situ sulfidation.15,16,18,19 At Tn values such as 600 °C (Figure 2d,i) we obtain films that are essentially a monolayer of ∼100 nm diameter FeS2 grains, a desirable microstructure for PV applications. At even higher Tn (e.g., 700 °C, Figures 2e,j) discontinuity and delamination

![Figure 1. X-ray Diffraction Characterization.](image)
occur.23 This is in the temperature range at which pyrite decomposition is likely to become an issue under these conditions. The transport studies that are the major focus of this paper thus focus on 200 °C ≤ T_s ≤ 600 °C.

Quantification of the results from Figure 1 and 2, and additional characterization data, are shown as a function of T_s in Figure 3, which plots (a) the lattice parameter (a) from WAXRD, (b) the normalized intensity of the (200) pyrite WAXRD peak (I_{200}), (c) the lateral grain size (d_{grain}) from SEM, (d) the film thickness (t) from tilted SEM, and (e) the S content from EDS. The out-of-plane lattice parameter (Figure 3a) is expanded by ∼0.5% with respect to bulk (horizontal dashed line). Variations in lattice parameter have been reported for multiple FeS deposition methods [e.g., refs 16, and 24], and could be related to point defects,16 or, potentially, strain. We note, (i) that the expansion observed here is comparable in magnitude to other work24 and (ii) that our data provide evidence of an approach to the bulk value above 400 °C, perhaps implying lower defect density or the onset of strain relaxation. Panels b and c illustrate more quantitatively the trends in Figures 1 and 2, a substantial increase in I_{200} and d_{grain} occurring above T_s ≈ 400–450 °C. As can be seen from Figure 3d, the final film thicknesses are essentially independent of T_s above 200 °C, the expansion factor (∼3.4) lying close to theoretical estimates for Fe to FeS conversion, again consistent with nominally phase-pure FeS_2. Finally, from Figure 3e it is seen that the S content is only weakly T_s-dependent. Some evidence for S excess is found at 200 °C < T_s < 400 °C, perhaps consistent with the expanded lattice parameter (Figure 3a). Additional characterization for 200 °C ≤ T_s ≤ 600 °C is provided in the Supporting Information, demonstrating a uniform Fe:S ratio through the film depth (from Auger electron spectroscopy (AES)), in addition to further evidence of phase purity (from Raman).

Wide temperature range measurements of the resistivity (ρ) for 200 °C ≤ T_s ≤ 600 °C are shown in Figure 4a on a log—linear plot. Although all ρ(T) curves exhibit monotonic semiconducting-like behavior, the evolution with T_s is nontrivial. Specifically, for T_s ≤ 450 °C
Figure 4. Temperature-dependent resistivity behavior. Temperature dependence of the resistivity ($\rho$) of 110 nm-thick FeS$_2$ films sulfided at temperatures of 200–600 °C. The data are plotted as (a) $\rho$ (log scale) vs $T$ (all films), (b) $\ln \rho$ vs $T^{-1/2}$ (for sulfidation temperatures 500 °C and below), and (c) $\ln \rho$ vs $T^{-1}$ (for sulfidation temperatures 550 °C and above). (d) $\ln W$ vs $\ln T$ is plotted in the low $T$ region, where $W = -d \ln \rho / d \ln T$. Slopes of $m = 1/2$ and 1 are shown for comparison, where $m$ is the exponent in $\rho = \rho_0 \exp(T_\sigma/T)^m$. The curves have been vertically displaced for clarity.

both the low and high $T$ values of $\rho$ increase monotonically with $T_s$, while for $T_s > 450$ °C the 300 K $\rho$ values saturate, but the low $T$ resistivity actually decreases with increasing $T_s$. This is depicted more clearly in Figure 5a. We immediately note the obvious correlation with the structural data (Figure 3), specifically the importance of the 450 °C temperature scale. Figure 4b,c demonstrate that this abrupt change in resistivity behavior at $T_s \approx 450$ °C is in fact due to a change in the functional form of $\rho(T)$. Lower $T_s$ samples (Figure 4b) exhibit linear behavior at low $T$ on a $\ln(\rho)$ vs $T^{-1/2}$ plot, implying a $T$ dependence of the form $\rho = \rho_0 \exp(T_\sigma/T)^{1/2}$, where $\rho_0$ is the $T \to \infty$ value of $\rho$, and $T_\sigma$ is a characteristic temperature. In contrast, higher $T_s$ samples (Figure 4c), particularly the 600 °C limiting case, approach linearity at low $T$ on a $\ln(\rho)$ vs $T^{-1}$ plot, implying a simple activated dependence, $\rho = \rho_0^A \exp(E_s/k_B T)$, where $\rho_0^A$ is the $T \to \infty$ value of $\rho$, and $E_s$ is the activation energy. This conclusion is reinforced via a quantitative, unbiased analysis using the logarithmic derivative method, where $w = -d(\ln(\rho))/d(\ln T)$ is plotted vs $\ln T$ in order to linearize $\rho = \rho_0^A \exp(T_\sigma/T)^m$, yielding the exponent, $m$, from the slope. This is shown in the low $T$ region, in Figure 4(d), where slopes of $m = 1/2$ and 1 are also shown for comparison. The crossover from $m \approx 1/2$ to $m \approx 1$ with increasing $T_s$ is clear, the separatrix between the two regimes lying around 450 °C. This is shown more explicitly in Figure 5b, where the $T_s$ dependence of the best-fit value of $m$ at low $T$ is plotted. It must be emphasized that we are focusing here on the low $T$ asymptotic behavior. As shown in Figure 4b,c, and discussed in more detail below, deviations from these forms do occur at higher $T$, and are in fact expected. Figure 5 panels c and d further plot the $T_s$ dependence of the parameters $\rho_0$, $T_\sigma$, and $\rho_0^A$, from the low $T_\sigma$ and high $T_s$ regions, respectively. In all cases the crossover at 400–450 °C is quite clear.

The central question at this stage is the origin of the low $T_s$ ($m \approx 1/2$) and high $T_s$ ($m \to 1$) low temperature transport behavior, and indeed the crossover between the two. Straightforwardly, we interpret the simple activated ($m \approx 1$) behavior approached at high $T_s$ in terms of conventional semiconductor transport, likely associated with shallow dopants or band-tail conduction. The $E_s$ values (~5 meV) are consistent with this interpretation, as is the order of magnitude of $\rho_0^A$ (ref 27). Given the small values of $E_s$ the curvature seen in Figure 4c at higher $T$ is unsurprising and indicates a gradual crossover to higher activation energy transport at higher $T$, as would be expected. The $m = 1/2$
behavior at low $T_S$ is more challenging. This behavior could be interpreted in terms of Efros-Shklovskii variable-range hopping (ES VRH).\textsuperscript{27} In ES VRH, the Coulomb interaction effects result in a soft-gapped density of states around the Fermi energy leading to $\rho = \rho_0 \exp\left(\frac{T_D}{T}\right)^{1/2}$, with $T_D = 2.8e^2/(\kappa_kT_L)$, where $\kappa$ is the dielectric constant and $L_C$ is the carrier localization length.\textsuperscript{27}

However, an identical $T$ dependence also arises for thermally assisted tunneling between nanoscopic conductive regions embedded in a more insulating matrix (often referred to as inter-granular hopping (IGH)), due to the Coulomb energy penalty associated with single carrier charging.\textsuperscript{28,29} This mechanism must be explicitly considered here as such a nanoscale inhomogeneity in conductivity is certainly plausible, particularly in polycrystalline films synthesized via a diffusion-limited reaction with sulfur. IGH has even been employed as a method to detect such inhomogeneity.\textsuperscript{30} We argue below that a strong case can in fact be built in favor of the IGH scenario over ES VRH. Note that in either case (VRH or IGH), a gradual crossover to other forms (of nonhopping) conduction is expected in the higher $T$ limit.

The first point in favor of IGH is that the observed $T_D$ values are difficult to reconcile with ES hopping. In ES VRH the maximum $T_D$ occurs in the insulating limit, where $\kappa$ has no electronic enhancement and $L_C$ takes its limiting value, the Bohr radius.\textsuperscript{27} Using literature values for $\kappa$ (ref 31) and the effective mass,\textsuperscript{32} and a hydrogenic model for the Bohr radius, we obtain $T_D \approx 1800$ K for n-type\textsuperscript{33} FeS$_2$. At higher doping $\kappa$ and $L_C$ diverge as the insulator–metal transition is approached, rapidly decreasing $T_D$ (ref 27). In disordered polycrystalline films that are anticipated to be heavily doped (as confirmed below) we thus expect $T_D \ll 1800$ K.

As can be seen from Figure 3d this is not the case; $T_D$ lies in the 1000–2000 K range. A second strong argument against ES VRH is provided by magnetoresistance (MR) measurements, as detailed in the Supporting Information. In perpendicular fields diamagnetic wave function shrinkage leads to rapid decreases in wave function overlap with increasing magnetic field ($H$) (ref 27), and thus to large positive MR. This MR follows $\ln(\rho(H)/\rho(0)) = t(e/\hbar)^2H^2L_C^2(T/T_D)^{-1.5}$ for ES VRH in the weak field limit, with $t = 0.0015$ (ref 27). We thus expect, as has been verified in numerous systems,\textsuperscript{27} a large positive MR, growing monotonically with decreasing $T$ and increasing $H$. As shown in the Supporting Information, this is not the case in our films. While the MR is positive at $T_S = 400$ °C, its $T$ dependence is qualitatively inconsistent with expectations, saturating at $\approx 1.5\%$ at 15 K. This discrepancy between experiment and ES VRH theory is even more acute for films synthesized at $T_S = 200$ °C, where the MR is nonmonotonic with $T$, has a complex $H$ dependence, and even changes sign below 10 K. In short, both the energy scale associated with $\rho(T)$ and the behavior of $\rho(T,H)$, are inconsistent with ES VRH.

On the basis of the above, interpretation of $\rho = \rho_0 \exp\left(\frac{T_D}{T}\right)^{1/2}$ behavior in terms of IGH is clearly favored, directly implicating nanoscale spatial variations in conductivity. Given our diffusion-limited synthesis conditions one obvious scenario is the retention of nanoscopic conductive S-deficient cores (of Fe, Fe$_{1.5}$S$_{3-x}$ or Fe$_2$S$_4$ (ref 34), with volume fractions beneath WAXRD detection limits, at the center of nominally stoichiometric FeS$_2$ grains. Magnetometry provides a sensitive probe of such a possibility as the Fe$^{2+}$ in FeS$_2$ exists in a non-magnetic ($S = 0$, $t_{2g}^6e_g^0$) configuration [see ref 26 for example], whereas Fe, Fe$_{1.5}$S$_x$ and Fe$_2$S$_4$ exhibit magnetic order. Magnetization ($M$) vs $H$ loops were thus collected on $T_S = 200$ and 400 °C samples (insets to Figure 6a,b). Remarkably, the 200 °C film exhibits clear ferromagnetic response, with finite remanence and coercivity, and a small but significant saturation magnetization of $0.04\mu_B$/Fe. The main panel of Figure 6a displays $M(T)$ measured at $H = 100$ Oe (after both field cooling (FC) and zero field cooling (ZFC)), demonstrating superparamagnetic behavior. The ferromagnetism is thus not uniformly distributed but is confined to small volumes. These volumes apparently become thermally unstable (on the time scale of the measurement) at a blocking temperature, $T_B$, around 78 K.
Assuming for the moment that this magnetic signal arises due to metallic Fe, the magnetization we observe can be accounted for by as little as 0.5 vol % of unreacted Fe, a value that lies below our own WAXRD detection limits (see Supporting Information for more details), and likely many such lab XRD systems. Combining this estimated volume fraction with the measured grain boundary diffusion (assuming grain boundary widths of 1 and 10 nm), 16 and for large grain polycrystal 16 and single crystal Fe 57 (to exemplify bulk diffusion). The shaded region on the left (right) marks the range of relevant thicknesses (grain sizes).

Figure 6. Magnetometry and sulfur diffusion. Panels a and b show the measuring temperature (T) dependence of the magnetization of 110 nm-thick FeS2 films sulfided at 200 and 400 °C. The data were acquired in H = 100 Oe after zero field cooling (ZFC) and field cooling (FC) in 100 Oe. The insets show 10 K hysteresis loops. Panel c displays the temperature dependence of the diffusion length (δs = D(T2δs)1/2, where D(T2δs) is the diffusion coefficient and t is time (fixed at 8 h)), for S diffusion in Fe. The data are shown both for grain boundary diffusion (assuming grain boundary widths of 1 and 10 nm), 16 and for large grain polycrystal 16 and single crystal Fe 57 (to exemplify bulk diffusion). The shaded region on the left (right) marks the range of relevant thicknesses (grain sizes).
CONCLUSIONS

We conclude with some comments on the implications of these findings for future research on FeS2 for PV applications. First, and particularly for synthesis routes that may result in diffusion limited conditions, it is clear from this work that attainment of conventional diffusive semiconductor transport in FeS2 films is nontrivial, requiring significant attention to nanoscale chemical homogeneity. Second, it is also clear that considerable caution must be exercised in the interpretation of Hall measurements, particularly with respect to the determination of the sign of the charge carriers. In this context we note (i) that some reports of p-type conduction in FeS2 films have been made in the absence of temperature-dependent measurements definitively establishing diffusive transport, and (ii) that an intriguing correlation exists, both in bulk and thin film FeS2, between low mobility and apparent p-type transport. With regard to the latter, recent work on single crystals has even revealed a temperature-dependent sign reversal of the Hall effect.35 Future work, combining a variety of synthesis methods with detailed electronic characterization, should be able to resolve many of these issues, hopefully providing the long-elusive understanding of the doping and transport mechanisms in FeS2 films. On this note we would like to point out that while the mobilities reported in this paper for ex situ sulfidized films remain modest (~1 cm2 V−1 s−1 or less), considerable room for improvement remains, particularly by improving synthesis and postdeposition treatment protocols. Indeed, future work refining synthesis and processing techniques for appropriate defect management will be required to reduce the carrier densities to workable levels for PV devices, and to improve mobility. The origin of the n-type behavior seen in this work is also an open issue that will require further work. While there are many possible origins, uncontrolled dopants in the Fe starting material, and out-diffusion of dopants from the substrate are obvious possibilities that should be further investigated.

METHODS

FeS2 thin films were fabricated via ex situ sulfidization, as detailed in the Supporting Information. Briefly, sputtered Al2O3 (0001)/Fe(110) films (33 nm thick, deposited at 300 °C) were placed in quartz tubes (8 cm3 volume) with 1.0 ± 0.1 mg of 99.999% pure S, evacuated to 1 × 10−4 Torr, sealed, and heated for 8 h at a sulfidation temperature, T, between 100 and 800 °C. Simple calculations (see SI for more details) give a resulting S vapor pressure of 2 Torr at 200 °C, 25 Torr at 400 °C, and 45 Torr at 700 °C. After synthesis, the films were thoroughly characterized structurally and chemically (see Supporting Information for details) via wide-angle X-ray diffraction (WAXRD), scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS), depth-profiled auger electron spectroscopy (AES), and Raman spectroscopy. Electronic transport (see Supporting Information for details) employed in contacts in a 4-wire van der Pauw configuration using ac (13.7 Hz) and dc excitation. Measurements were made from 5–300 K, in magnetic fields up to 9 T, with extensive checks for Ohmicity, contact resistance, and self-heating. More details are provided in the Supporting Information. Magnetometry was done in a SQUID magnetometer from 5–300 K in fields to 7 T.

Conflict of Interest: The authors declare no competing financial interest.

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Supporting Information Available: Additional film synthesis details, additional structural characterization data from X-ray diffraction, Auger electron spectroscopy and Raman spectroscopy, additional transport and magnetotransport data, additional Hall effect data, and additional information on magnetometry measurements and associated analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

REFERENCES AND NOTES


42. For such a simple estimate, the length scale relevant for the grain boundary diffusion is the film thickness, which is 33 nm initially, rising to 110 nm after sulfidation. The length scale relevant for the bulk diffusion is the grain size, which is in the range 55 to 110 nm.

