Transport Evidence for Sulfur Vacancies as the Origin of Unintentional n-Type Doping in Pyrite FeS₂

Bryan Voigt,‡ William Moore,‡ Michael Manno,‡ Jeff Walter,‡,∥ Jeff D. Jeremiason,⁎,† Eray S. Aydil,⁎,†,‖ and Chris Leighton⁎,†

†Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455, United States
‡Department of Physics and Astronomy, Carleton College, Northfield, Minnesota 55057, United States
§Department of Chemistry, Gustavus Adolphus College, Saint Peter, Minnesota 56082, United States
¶Department of Chemical and Biomolecular Engineering, New York University Tandon School of Engineering, Brooklyn, New York 11201, United States

ABSTRACT: Pyrite FeS₂ has long been considered a potential earth-abundant low-cost photovoltaic (PV) material for thin-film solar cells but has been plagued by low power conversion efficiencies and open-circuit voltages. Recent efforts have identified a lack of understanding and control of doping, as well as uncontrolled surface conduction, as key roadblocks to the development of pyrite photovoltaics. In particular, while n-type bulk behavior in unintentionally doped single crystals and thin films is speculated to arise from sulfur vacancies (Vs), proof remains elusive. Here, we provide strong evidence, from extensive electronic transport measurements on high-quality crystals, that Vs are deep donors in bulk pyrite. Otherwise identical crystals grown via chemical vapor transport under varied S vapor pressures are thoroughly characterized structurally and chemically, and shown to exhibit systematically different electronic transport. Decreased S vapor pressure during growth leads to reduced bulk resistivity, increased bulk Hall electron density, reduced transport activation energy, onset of positive temperature coefficient of resistivity, and approach to an insulator–metal transition, all as would be expected from increased Vs donor density. Impurity analyses show that these trends are uncorrelated with metal impurity concentration and that extracted donor densities significantly exceed total impurity concentrations, directly evidencing a native defect. Well-controlled, wide-range n-doping of pyrite is thus achieved via the control of Vs concentration, with substantial implications for photovoltaic and other applications. The location of the Vs state within the gap, the influence of specific impurities, unusual aspects to the insulator–metal transition, and the influence of doping on surface conduction are also discussed.

KEYWORDS: solar cells, photovoltaic absorbers, crystal growth, semiconductors, doping, defects, electronic transport, sulfur vacancies, insulator–metal transition

1. INTRODUCTION

Pyrite structure FeS₂ is a potentially ideal photovoltaic (PV) material for sustainable, low-cost, large-scale solar-to-electric energy conversion as it is composed of earth-abundant, nontoxic, inexpensive elements, has a band gap near the Shockley–Queisser maximum¹ (0.95 eV), and absorbs visible light so well that a 100 nm thick film absorbs >90% of sunlight.² These properties, combined with a room-temperature electron mobility³ of up to 360 cm² V⁻¹ s⁻¹ and minority carrier diffusion lengths (100–1000 nm) exceeding the thickness for complete light absorption,² led to the identification of FeS₂ in the 1980s as a promising material for thin-film solar cells. Attempts to employ FeS₂ as the absorber in Schottky,⁴ photoelectrochemical,⁵,⁶ and p–i–n-type⁷ solar cells all failed, however, due to low open-circuit voltages (VOC < 0.2 V) and power conversion efficiencies (<3%),² the latter falling an order of magnitude below the theoretical maximum.¹ These outcomes limited the interest in pyrite PV in the 1990s.

Around 2009, interest in FeS₂ grew, however, motivated by sustainability concerns with commercial thin-film solar cell absorbers such as CdTe and Cu(In,Ga)Se₂.⁸ Importantly, several efforts in this second wave of interest in pyrite have focused on fundamental reasons for poor PV performance.⁹–¹⁴ Three main issues have been identified: the possibility of deleterious secondary phases,¹¹,¹² surface conduction phenomena,¹³,¹⁴ and a lack of understanding and control of doping.¹³,¹⁴,¹⁶ Most recently, however, concerns over secondary phases such as pyrrhotite Fe₁₋ₓS and the FeS₂ polymorph marcasite have abated due to syntheses resulting in rigorously deleterious secondary phases,¹¹,¹² surface conduction phenomena,¹³,¹⁴ and a lack of understanding and control of doping.¹³,¹⁴,¹⁶

Received: January 21, 2019
Accepted: April 10, 2019
nanocrystals. Progress has also been made in understanding FeS$_2$ surfaces, particularly with respect to electronic behavior. In high-quality nominally undoped pyrite single crystals, for example, recent work unambiguously established surface conduction, where a surface layer shunts the semiconducting interior at low temperature ($T$) in conventional ("horizontal") resistivity ($\rho$) measurements. The surface conductive layer (which is two-dimensional and nanoscopic) is also commonly p-type, in contrast to the n-type bulk. This surface inversion correlates strikingly with X-ray photoelectron spectroscopy (XPS), which suggests pinning of the surface Fermi level near the valence band edge (along with the requisite band bending), providing a viable explanation for the low $V_{OC}$ plaguing pyrite PV devices. Though not fully understood, intrinsic surface states have been hypothesized as the origin of such surface electronic phenomena. Diversity in surface conduction in as-grown crystals and the effects of polishing/surface treatment remain to be understood, however, and mitigation of surface states stands as a major challenge.

Understanding and controlling doping, the third main issue noted above, has also seen recent progress, exemplified by the first explanation for the pyrite "doping puzzle". This refers to the fact that unintentionally doped pyrite single crystals are almost always n-type, whereas unintentionally doped thin films are typically reported p-type. A resolution to this puzzle was recently arrived at via a study of majority carrier type in FeS$_2$ crystals and films, using both Hall effect and thermopower. Zhang et al. demonstrated that not only pyrite single crystals but also sufficiently high-quality thin films are unambiguously n-type. Only in low electronic quality films, below $\sim1$ cm$^{-2}$ V$^{-1}$ s$^{-1}$ mobility ($\mu$), was p-type conduction evidenced. The crossover in Hall and Seebeck coefficients was shown to be directly correlated with the onset of hopping conduction, however, which is known to suppress and even invert the sign of Hall and Seebeck coefficients. The apparent p-type behavior at low $\mu$ was thus understood as an artifact of hopping, establishing predominance of n-type behavior in unintentionally doped FeS$_2$ crystals and films. The $\mu(n)$ relation (where $n$ is the Hall electron density) was additionally found universal in crystals and films, hinting at a common unintentional n-dopant.

With respect to the identity of this unintentional n-dopant, recent transport studies of high-quality nominally undoped pyrite crystals are again relevant. Those works reported exclusively n-type bulk behavior, with $n \approx 10^{15}$–$10^{17}$ cm$^{-3}$, deduced donor densities $N_D \approx 10^{19}$–$10^{20}$ cm$^{-3}$, and transport activation energies ($\Delta E$, from Arrhenius analysis of $n(T)$) of 170–230 meV, evidencing a deep donor. Moreover, in one study, the deduced total impurity concentration of $\sim35$ ppm (including Co, likely the only element unambiguously known to n-dope FeS$_2$) was found to be substantially below the extracted $N_D$ of $9 \times 10^{18}$ cm$^{-3}$ (120 ppm). This implies a native defect, as opposed to an impurity. The S vacancy ($V_S$) is one obvious culprit as, naively, $V_S$ (in Kröger–Vink notation) could be expected to electron dope FeS$_2$. $V_S$ have in fact long been hypothesized as important in n-doping of pyrite or even to be the specific origin of the low $V_{OC}$ in solar cells, but proof remains lacking.

The first evidence for substantial $V_S$ concentrations in bulk FeS$_2$ came from measurements of S deficiency using spectrometry and X-ray diffraction (XRD). $S/Fe$ ratios of single crystals determined from inductively coupled plasma atomic emission spectrometry were found to be $<2.0$, for example, the authors concluding FeS$_{2-x}$ with $x$ up to 0.06–0.24. These measurements involved dissolving crystals, however, which Luck et al. noted could lead to $S$ evaporation/outgassing. Refinement of XRD data and ensuing lattice parameter determinations were also interpreted in terms of high $V_S$ concentrations, although increased $\Delta E$ yielded smaller lattice parameters, opposite to many compound semiconductors. In addition to these studies on bulk $V_S$, there is also work identifying and characterizing $V_S$ formation on FeS$_2$ surfaces. In particular, a feature in $S$ 2p XPS spectra that strengthens with ion sputtering and/or vacuum annealing has been attributed to a surface S monomer in FeS$_2$, requiring the formation of $V_S$.

While a body of experimental evidence thus supports the formation of $V_S$ in substantial quantities in pyrite FeS$_2$ (particularly at the surface but also in the bulk), and points to a native defect as the deep donor in unintentionally doped crystals, the key evidence tying $V_S$ to bulk n-doping remains elusive. In addition, while these studies provide evidence of substantial $V_S$ concentrations in pyrite, this is not easily reconciled with theory. Specifically, multiple density functional theory (DFT) studies have found $\Delta H_{VS}$ values that are too high to result in significant $V_S$ concentrations, although such formation energies can be overestimated in DFT. Some DFT studies have additionally found that $V_S$ should not act as efficient donors in pyrite. Based on the above, a detailed study linking $V_S$ formation to bulk electronic properties and doping in FeS$_2$ is long overdue. Recent work refining the growth of high-quality phase-pure crystals and establishing majority carrier types lays a foundation for such an effort.

Here, we provide the strongest evidence to date that $V_S$ are indeed the dominant n-dopants in unintentionally doped FeS$_2$. This is derived from bulk electronic transport behavior in thoroughly characterized high-quality crystals grown via chemical vapor transport (CVT). Systematically varied S concentrations yield an electrically active monomer in FeS$_2$, long overdue. Recent work refining the growth of high-quality phase-pure crystals and establishing majority carrier types lays a foundation for such an effort.
2. EXPERIMENTAL SECTION

2.1. Potential Approaches To Control \( V_S \) Density in Pyrite \( FeS_2 \). Two potential approaches to control \( V_S \) densities in \( FeS_2 \) single crystals are to control \( S \) vapor pressures during growth (and on cooling) or to perform postgrowth annealing in a controlled atmosphere. In oxide semiconductors, for example, postsynthesis annealing under reducing conditions is commonly employed to control locally a vacancy defect (as in \( SrTiO_3 \), \( BaSnO_3 \), \( TiO_2 \), \( InO \), etc.). In \( FeS_2 \), however, \( S \) diffusion is slow, with a self-diffusion coefficient (\( D \)) of \( \sim 10^{-24} \) m\(^2\) s\(^{-1}\) at \( 400 \) °C.\(^6\) Moreover, decomposition to \( Fe_1-x S \) pyrrhotite phases during vacuum annealing begins at low temperatures, as low as \( 160 \) °C on the surface and \( 430 \) °C in bulk.\(^7\) It is thus not clear whether \( S \) outdiffusion during reduction can dominate decomposition to pyrrhotite. Quantitative comparison of these processes is therefore provided in the Supporting Information (Section A, Figure S1). Using reported \( D(T) \) values,\(^8\) \( S \) diffusion lengths (\( l \approx \sqrt{\alpha \cdot T} \)) for 24 h time (\( t \)) periods reach only 2 nm at temperatures up to \( 430 \) °C, above which decomposition to \( Fe_1-x S \) proceeds rapidly.\(^9\) Only a very thin \( FeS_2 \) surface layer could thus be expected at workable vacuum-annealing temperatures. In fact, even at \( T \lesssim 430 \) °C decomposition likely dominates. Specifically, the rate of the \( FeS_2 \rightarrow Fe_1-x S \) transformation under vacuum has been modeled by Lambert et al. for \( T > 430 \) °C.\(^6\) Extrapolation to \( T \leq 430 \) °C predicts the formation of \( 10^{-10} \) nm thick \( Fe_1-x S \) surface layers in 24 h, 3 orders of magnitude larger than the \( S \) diffusion length (Supporting Information, Figure S1). We have verified this, observing \( \sim 10^4 \) nm thick \( Fe_1-x S \) skins on the surface of \( FeS_2 \) crystals after vacuum annealing at \( 380 \) °C. While \( V_S \) may accelerate \( S \) diffusion, the 6-order-of-magnitude increase in \( D \) required to compete with decomposition (Supporting Information Section A) is unlikely. Postgrowth annealing in reducing atmosphere is therefore not a promising route to control \( V_S \) in bulk \( FeS_2 \) crystals.

In this work, we thus pursue the second approach, i.e., controlling \( S \) vapor pressure during growth (and on cooling) to control \( V_S \) densities. One advantage, allowing for kinetic trapping of \( V_S \) during growth.

2.2. Materials and Methods. Unintentionally doped pyrite \( FeS_2 \) single crystals were grown via CVT.\(^10\) Cylindrical quartz ampoules (50 cm\(^3\)) were first cleaned by sonication in deionized water, acetone, and methanol, and dried at 400 °C. Ampoules were then loaded with 100 mg of \( FeBr_2 \) transport agent (Sigma-Aldrich, 99.9999% purity) and 2.2 g of pyrite \( FeS_2 \) precursor powder, evacuated to \( 10^{-6} \) Torr and flame-sealed. Both commercial (Alfa Aesar, 99.9% purity) and laboratory-synthesized \( FeS_2 \) precursor powders were used, hereafter referred to as “standard” and “high-purity”, respectively. High-purity \( FeS_2 \) was synthesized by reacting \( S \) (Alfa Aesar, 99.9995% purity) and \( Fe \) (Alfa Aesar, 99.998% purity) in evacuated ampoules (6:1 \( S/Fe \) molar ratio) for 6 days at 500 °C. The resulting powder was ground and repeatedly sultidized until phase-pure pyrite \( FeS_2 \) was obtained, verified by powder X-ray diffraction (PXRD). Key for this study, the \( S \) vapor pressure during CVT crystal growth, was controlled via the \( S/Fe \) molar ratio loaded in the ampoules, hereafter referred to as the “\( S/Fe \) loading”. We emphasize that this is the molar ratio of precursors in the CVT growth, not the \( S/Fe \) ratio of resultant crystals. To increase \( S/Fe \) loading above 2.0, excess \( S \) powder (Alfa Aesar, 99.9995% purity) was added. To decrease \( S/Fe \) loading below 2.0, high-purity \( FeS_2 \) precursor was partially decomposed in \( N_2 \) at 600 °C to form controlled fractions of pyrrhotite \( Fe_1-x S \). The molar % of each phase was estimated from PXRD (using pyrite\(^{11,12} \) and pyrrhotite\(^{13,14} \) reference patterns). Sealed ampoules were then placed in a two-zone furnace with precursors at one end (the source zone). During growth, the source and growth zones were maintained at 670 and 590 °C, respectively. An inverted temperature configuration was used for the first 3 days, to “clean” the growth zone,\(^15\) followed by 17 days of growth. The average growth rate was determined by normalizing the average masses of the 10 largest crystals from each ampoule by the growth duration.

Based on the above conditions, \( S \) vapor pressures during growth can be estimated to be 0.003 and 3.5 atm at low (<2.0) and high (3.0) \( S/Fe \) loadings, respectively. This was done using ideal gas behavior at high \( S/Fe \) loading, assuming \( S_2 \) as the primary species. At low \( S/Fe \) loading, considering likely gas-phase equilibria in this CVT process and ignoring \( S \) vapor from \( FeS_2 \) decomposition, we estimate the \( S \) vapor pressure from the \( FeBr_2 \) vapor pressure. The uncertainty in this estimate, and the lack of a simple method to directly measure the \( S \) vapor pressure during growth, is the main motivation to simply use \( S/Fe \) loading as the primary variable in this study. It would be ideal to directly correlate transport properties with an actual \( V_S \) concentration, but in the absence of any clear means to do this at the semiconductor doping levels relevant to this work, \( S/Fe \) loading is the best choice variable.

To check phase purity in representative crystals, synchrotron PXRD (\( I = 0.412744 \) Å) was performed in capillary transmission mode at beamline 11-BM of the Advanced Photon Source, Argonne National Laboratory. For each crystal growth, the lattice parameter \( a \) was determined from Bragg–Brentano PXRD on a Rigaku MiniFlex 600 with a Cu source and graphite diffracted beam monochromator. A linear fit of \( a \) vs cos\( ^{1/2} \)θ/sinθ was employed.\(^16\) High-resolution single crystal X-ray diffraction (SCXRD) data, including rocking curves (RCs), were collected on a Panalytical X’Pert Pro with monochromated Cu Kα radiation. The crystal \( S/Fe \) ratio (not the \( S/Fe \) growth loading (see above)) was determined from energy-dispersive spectroscopy (EDS) on a \(~1\) mm\(^2\) spot in a JEOL JSM-6010PLUS/LA scanning electron microscope with an internal JEOL X-ray detector. For impurity analysis, particle-induced X-ray emission (PIXE) was done on a National Electrostatics Corporation (NEC) MAS 1700 pellotron tandem ion accelerator with a 4000 keV He\(^{++} \) ion beam and a Kevex Si drift detector (Model 3700 with a 0.7 mm thick Be window), coupled with a 25 μm thick Al filter for X-ray detection. PIXE data were analyzed using the software package GUPiX,\(^17\) trace metal detection limits were 10–100 ppm, depending on the element. Additional impurity analysis employed inductively coupled plasma mass spectrometry (ICPMS). Crystals of >15 mg were ground and digested in 10 mL ULTREX II nitric acid. An aliquot of digestate was diluted with ultrapure Milli-Q water prior to the addition of internal standard (Inorganic Ventures ICPMS-71D) and then analyzed using an Agilent 7700.

Crystals were prepared for SCXRD and electrical transport by first identifying a [111] or [100] facet by crystal habit and then polishing from both sides. Polishing entailed progressive grinding down to 1200 grit SiC paper, followed by polishing with 3 and 1 μm diamond slurries. Soldered In or sputtered Al/ Au contacts were then placed on polished facets in the van der Pauw geometry. Four terminal resistances were measured DC with a Keithley 2400 or a combination of a Keithley 220 current source and a Keithley 2002 voltmeter. Low-temperature (below ~100 Ω) were typically measured AC with a Linear Research LR-700 resistance bridge (16 Hz). Frequent checks were made for ohmicity, contact resistance, and self-heating. Most measurements were made in a Quantum Design Physical Property Measurement System (PPMS) with a 9 T superconducting magnet between 1.8 and 400 K. Additional measurements were made in a closed-cycle refrigerator and a liquid \( N_2 \) flow cryostat, both with 1 T electromagnets.

3. RESULTS AND DISCUSSION

3.1. Structural and Chemical Characterization. CVT growth resulted in [111]- and [100]-faceted crystals, with dimensions of up to 7 mm, as illustrated in an inset in Figure 1c. Figure 1a shows the synchrotron PXRD pattern from a ground crystal grown at S:Fe loading of 1.69, the lowest loading investigated here. Such conditions provide the most stringent test for phase purity, as the formation of pyrrhotite \( Fe_1-x S \) becomes of highest concern at S:Fe loadings of <2.0. All peaks can nevertheless be indexed to pyrite (reference pattern\(^18\) shown in Figure 1b), although a trace of \( \alpha-SiO_2 \) is evidenced (asterisk in Figure 1a). The latter is attributed to shards of quartz from breaking open the growth ampoule.
resulting in minor contamination of ground crystals (which is of no concern for measurements on bulk crystals). The extracted \( a \) is \( 5.4165 \pm 0.0014 \) Å, in agreement with the literature.\(^{9,26,41,64,69-71}\) High-resolution SCXRD from a representative \((111)\)-faceted, polished crystal is shown in Figure 1c, exhibiting only 111 and 222 reflections, confirming single crystallinity. The RC through the 111 peak (Figure 1c, inset) has a full width at half-maximum (FWHM) of only 0.0061°, \( \sim 3 \) times the instrumental resolution, and within a factor of \( \sim 3 \) of the lowest reported value for pyrite.\(^7\) This indicates a low mosaic spread and thus a low overall defect density.

Chemical characterization of representative crystals grown from standard purity precursor (at an example S:Fe loading of 1.95) was performed with EDS and PIXE, as shown in the Supporting Information (Section B, Figure S2). Disregarding typical surface O and C contaminations, only Fe and S are observed, the resulting S/Fe ratio of 1.97 ± 0.10 confirming the expected stoichiometry. In PIXE (Figure S2b), the suppression of Bremsstrahlung reduces impurity detection limits to \( \sim 10-100 \) ppm (compared to \( \sim 1 \) atom % in EDS). The crystal studied by PIXE in Figure S2b displays Fe and S core transitions, Fe escape and summation peaks, and detector artifact peaks\(^{15}\) but still no evident impurity peaks. In some crystals grown at S:Fe loadings of <2.4, however, and universally in those grown at >2.4, a shoulder is observed near 7.5 keV, which we assign to Ni. GUPIX analysis of 13 crystals grown at different S:Fe loadings with standard precursor indicates Ni concentrations of 50–360 ppm with a detection limit of \( \sim 50 \) ppm. Importantly, the certificate of analysis for the standard FeS\(_2\) precursor powder (Supporting Information Section B, Figure S3) indicates 514 ppm Ni; this is very likely the source of Ni in these standard purity crystals. Note that Br, which could incorporate from the FeBr\(_2\) transport agent, was not detected in any of our PIXE spectra to an estimated sub-100 ppm limit of detection. Additional time-of-flight secondary ion mass spectrometry was able to detect a low-level Br signal but with no systematic dependence on S:Fe loading.

To obtain a broader, higher sensitivity picture of impurity incorporation, ICPMS was performed. Of the detected elements, Na, Mg, Al, K, Ca, Zn, As, Se, Cd, and Sn were not quantified due to very low count rates or inconsistent backgrounds/standards. V, Ga, Rb, Sr, Ag, Sb, Cs, Ba, Pb, Th, and U were also detected but at sub-ppm average

Table 1. Growth Rates and Impurity Concentrations (as Determined by ICPMS) in Representative FeS\(_2\) Crystals Grown at Various S:Fe Loadings\(^9\)

<table>
<thead>
<tr>
<th>S:Fe loading</th>
<th>growth rate (mg per day)</th>
<th>Ti (ppm)</th>
<th>Cr (ppm)</th>
<th>Mn (ppm)</th>
<th>Co (ppm)</th>
<th>Ni (ppm)</th>
<th>Cu (ppm)</th>
<th>total MBI (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.00</td>
<td>5.8</td>
<td>0.95 ± 0.14</td>
<td>16.07 ± 0.18</td>
<td>0.55 ± 0.07</td>
<td>4.33 ± 0.08</td>
<td>87.8 ± 3.3</td>
<td>0</td>
<td>131</td>
</tr>
<tr>
<td>2.34</td>
<td>6.1</td>
<td>1.00 ± 0.19</td>
<td>44.03 ± 0.42</td>
<td>6.68 ± 0.26</td>
<td>9.20 ± 0.13</td>
<td>363.3 ± 3.6</td>
<td>0.55 ± 0.08</td>
<td>445</td>
</tr>
<tr>
<td>2.91</td>
<td>0.49</td>
<td>1.08 ± 0.15</td>
<td>44.08 ± 0.32</td>
<td>0.75 ± 0.08</td>
<td>6.11 ± 0.09</td>
<td>468.0 ± 3.5</td>
<td>0.76 ± 0.08</td>
<td>542</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Crystals Grown with Standard FeS(_2) Precursor Powder</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystals Grown with High-Purity FeS(_2) Precursor Powder</td>
</tr>
</tbody>
</table>

\(^9\)Crystals grown from standard and high-purity FeS\(_2\) precursor powders are shown at the top and bottom, respectively. The crystal growth rate (averaged over the 10 largest crystals in each ampoule) and concentrations of Ti, Cr, Mn, Co, Ni, Cu, and total metal-basis impurities (MBIs) are shown.
concentrations. Beyond this, Mo and Ge were found at average concentrations of 1.9 and 18 ppm, respectively, but with no dependence on S:Fe loading or precursor purity. More important are the transition metal species Ti, Cr, Mn, Co, Ni, and Cu, shown in Table 1 for crystals grown with standard (top) and high-purity (bottom) precursors, at various S:Fe loadings. Considering first the crystals grown from standard purity precursors, at a high S:Fe loading of 2.91, for example, we find 468 ppm Ni, 44 ppm Cr, 6 ppm Co, 1 ppm Ti, and <1 ppm Mn and Cu, giving a total metal-basis impurity (MBI) concentration of 542 ppm. Significantly, the dominant Ni impurity is found at levels approximately consistent with the concentration in the precursor FeS₂ (Figure S3), as well as PIXE, as discussed above. Of the other impurities, Co is particularly important as it is a known shallow donor in FeS₂. The 6 ppm in this crystal would correspond to n(300 K) = 4.5 × 10¹⁷ cm⁻³, assuming full dopant activation and no compensation. Detailed comparisons between the measured n and various impurity concentrations, including Co and Ni, are provided below in Section 3.2. Note for now that as the S:Fe loading is decreased to 2.34 and 2.00, the total MBI concentration in Table 1 decreases, eventually reaching 131 ppm, at which point Ni and Co reach 88 and 4 ppm, respectively. This trend is important, as it provides a means to distinguish impurity doping from VS doping. Specifically, based on Table 1, impurity doping would be expected to increase with increased S:Fe loading, whereas VS doping should decrease.

The origin of the lower total MBI concentration at lower S:Fe loading is likely the increased crystal growth rate, also shown in Table 1. Assuming fixed background vapor pressures of the species responsible for these impurities (from the FeS₂ precursor), defect concentrations incorporated in growing crystals would scale inversely with the growth rate. Although not quantified in this work, nonmetal impurities such as H and O, which could play a role in doping, are also likely to have densities that scale inversely with the growth rate. This is again inverse to the expected scaling with VS. Also significant in Table 1 is that crystals grown from high-purity precursors (bottom of Table 1) are indeed of higher purity, the total MBI concentration falling as low as 29 ppm. The dominant transition-metal impurities are now Cr (1−12 ppm) and Ni (3−5 ppm), the Ni being up to 2 orders of magnitude lower than in crystals from standard precursors. These Cr and Ni concentrations are similar to those reported in other crystals grown with the same (high-purity) Fe and S precursors. In Section 3.2 below, transport properties of standard and high-purity crystals are compared in detail.

Figure 2 shows how the S:Fe loading in the growth ampoule impacts the average crystal growth rate, the average resulting EDS S/Fe ratio, the lattice parameter, a, and the RC FWHM. For the growth rate and EDS S/Fe ratio, multiple crystals were measured from each batch and the error bars represent standard deviations; for a and the RC FWHM, the error bars represent total uncertainties. Note also that data are shown for crystals grown with both high-purity (Figure 2a−d, green points) and standard purity precursors (Figure 2e−h, red points). The first noteworthy point, already suggested by Table 1, is the rapid decrease in average growth rate at S:Fe loadings above ∼2.4 (in both Figure 2a,e), qualitatively consistent with prior FeS₂ CVT. Importantly, the data of Figure 2b,f show that the crystal S/Fe ratios are all 2.0 within uncertainty, independent of the S:Fe loading, with no detectable downturn at loadings below 2.0. This does not, of course, indicate negligible VS concentration at levels relevant to doping, due to the substantial EDS uncertainty (∼0.1 on the S/Fe ratio); it instead indicates that 1:2 stoichiometry is approximately maintained across the range of S:Fe loadings. This latter point is supported by PXRD data, which indicate phase-pure pyrite FeS₂ for all samples shown here. Resulting a values are plotted in Figure 2c,g with a range of prior single-crystal literature values (5.4170−5.4188 Å) shaded. There is no apparent dependence of a on S:Fe loading, and in all cases, the values lie at the lower end of the literature range. Defects commonly increase a, and we thus take this as a positive indication. In addition, any influence of VS on a is
apparently below the 0.001 Å level. Lastly, the RC FWHM (Figure 2d,h) demonstrates that mosaic spread is also independent of S:Fe loading, although there may be some minor reduction in crystals grown from high-purity precursors (mosaicity would generally be expected to decrease in higher-purity crystals). On aggregate, the data of Figure 2 demonstrate remarkably constant structural and chemical characterization parameters with S:Fe loading.

3.2. Electronic Transport: Evidence for V₅ as n-Type Dopants. Despite their structural similarity, the crystals discussed above display systematically varied electronic transport, the trends with S:Fe loading providing strong evidence that V₅ are deep donors in FeS₂. Figure 3 shows ρ(T) for multiple representative crystals grown at different S:Fe loadings from high-purity (top panel, Figure 3a) and standard purity (bottom panel, Figure 3b) precursors. Considering first the high-purity crystals, high S:Fe loadings such as 2.52 (lightest green line, Figure 3a) display ρ(T) now understood to be typical of unintentionally doped, polished FeS₂ crystals. Semiconducting behavior (i.e., large negative dρ/dT) occurs down to an inflection point at ∼225 K, where ρ(T) flattens. This is due to a crossover from bulk- to surface-dominated conduction, where carriers freeze out in the semiconducting interior upon cooling, eventually becoming shunted by the more conductive surface. As the current goal is to study how V₅ concentrations influence bulk transport, the surface-dominated region below ∼150–225 K (shaded in Figure 3) is not discussed further. We note only that the crossover to low T surface behavior evolves with S:Fe loading, becoming different in nature at low S:Fe, a point we will discuss elsewhere.

Most significant for the current work, the conduction at high T, in the bulk regime, changes dramatically as S:Fe loading decreases from 2.52 to 1.77 in Figure 3a. Specifically, ρ(300 K) decreases by over 2 orders of magnitude, while dρ/dT weakens and then inverts to metallic-like (i.e., dρ/dT > 0) transport. While bulk transport cannot be tracked to low T due to surface conduction, preventing the assessment of T → 0 behavior, this indicates phonon-limited transport and evolution toward an IMT with decreased S:Fe loading. Figure 3b reveals that this trend also occurs in standard purity crystals. These crystals have lower ρ(300 K), indicating that at least some of the MBI are dopants, but ρ(300 K) still decreases by an order of magnitude with decreased S:Fe loading, accompanied by inversion of high T dρ/dT. Much additional evidence is provided below, but we ascribe this behavior to increased V₅ concentrations trapped in FeS₂ crystals as the S:Fe loading (and thus S vapor pressure during growth) is decreased, leading to increased n-doping, decreased resistivity, and, eventually, metallic-like dρ/dT.

Additional evidence is provided in Figure 4, which plots the inverse T dependence of ρ, n, and μ for two representative high-purity crystals grown near the extremes of S:Fe loading...
(S:Fe loading of 1.69, left panel, Figure 4a-c, and S:Fe loading of 2.37, right panel, Figure 4d-f). As in Figure 3, the surface-dominated regime is shaded. Figure 4a,d first plots the resistivity (log scale), showing the sign change in high-temperature \(d\rho/dT\) with S:Fe loading, as expected from Figure 3a. Figure 4b,e then shows the 1/T dependence of the Hall electron density, \(n\), plotted on a log scale. As expected from the Introduction, all Hall signals in the bulk conduction regime in the crystals studied here are negative, indicating unintentional n-doping. Note the \(n(300\, K)\) value of \(\sim 2 \times 10^{15}\, cm^{-3}\) at S:Fe loading of 2.37 (Figure 4e), increasing by 2 orders of magnitude to \(\sim 2 \times 10^{17}\, cm^{-3}\) at S:Fe loading of 1.69 (Figure 4b), again consistent with increased \(V_s\) doping.

In terms of quantitative analysis of \(n(T)\), under the assumptions of nondegenerate statistics and negligible compensation, we expect

\[
n(T) = \frac{N_c N_D}{2} \frac{N_f}{N_a} e^{-\Delta E/k_BT} \tag{1}
\]

where \(N_c\) is the effective density of states in the conduction band, \(N_D\) is the donor density, \(\Delta E\) is the donor activation energy, and \(k_B\) is Boltzmann’s constant.\(^73\) In many semiconductors, however, particularly compounds, significant compensation is likely from impurities and/or nonstoichiometry-related defects. Under such conditions

\[
n(T) = \frac{N_c (N_D - N_a)}{N_a} e^{-\Delta E/k_BT} \tag{2}
\]

where \(N_a\) is the (compensating) acceptor density.\(^73\) Significantly, there is a factor of 2 difference in the exponents in eqs 1 and 2, generating a twofold difference in extracted \(\Delta E\) values. Consistent with recent work,\(^9\) we assume the compensated case and thus use eq 2; \(\Delta E\) values below would thus be twice as large if negligible compensation were assumed. In support of this assumption, note that high-purity crystals at high S:Fe loading have \(\sim 1\, ppm\) Co (Table 1) and that Co is a known shallow donor in pyrite.\(^35-38\) Full ionization would then produce an expected electron density of \(\sim 8 \times 10^{16}\, cm^{-3}\) due to Co alone, well above the lowest measured \(n(300\, K)\) \(\approx 3 \times 10^{15}\, cm^{-3}\), suggesting that compensation must be present. As discussed below, the behavior of the mobility with doping also provides evidence of compensation. Fe vacancies, among other defects, are one possible source. As illustrated by the solid line fits to eq 2 (Figure 4b,e), simple activated behavior is indeed observed at high \(T\) in both S:Fe loading limits, yielding \(\Delta E\) values of 17 and 220 meV, respectively. The donor activation energy thus decreases approximately 10-fold on decreasing S:Fe loading from 2.37 to 1.69, again consistent with \(V_s\) acting as donors in pyrite. A potential break to a lower activation energy process at lower \(T\) occurs in both cases (Figure 4b,e), but further analysis is hindered by proximity to the crossover to surface conduction at 200–300 K. We note that the extraction of \(N_D\) is in principle also possible from \(n(T)\) (using eq 2 with free electron estimates of \(N_c\) from \(m^*_e\)) but is complicated by the lack of knowledge of \(N_a\) as well as possibly degenerate transport at low S:Fe loadings. Analysis below thus focuses on extracted \(\Delta E\) values.

Figure 4c,f shows the Hall mobility, \(\mu(T)\), computed from \(\rho(T)\) and \(n(T)\). Both S:Fe loadings result in qualitatively typical behavior for moderately doped semiconductors, \(\mu\) first increasing on cooling from 400 K (due to phonon scattering), reaching a maximum value (\(\mu_{max}\)) at some \(T\) (\(T_{max}\)) and then falling at low \(T\) (due to ionized impurity scattering).\(^74\) Significant quantitative differences, however, appear in Figure 4c,f. \(\mu_{max}\) is \(\sim 60\, cm^2\, V^{-1}\, s^{-1}\) at a S:Fe loading of 2.37 (Figure 4f), occurring close to the upper limit of the measurement at 400 K. At a S:Fe loading of 1.69, however (Figure 4c), \(\mu_{max}\) increases almost 10-fold to \(\sim 550\, cm^2\, V^{-1}\, s^{-1}\), now occurring at \(\sim 200\, K\). A simple interpretation, supported by additional data below, is that these crystals, despite their overall quality, have a non-negligible density of background charged impurities (deep levels and acceptors), consistent with the suspicion of compensation. Under such circumstances, increased \(V_s\) doping at low S:Fe loading increases \(n\), better screening the scattering potential from the background charged impurities, thus increasing \(\mu_{max}\) and decreasing \(T_{max}\). Without these background charges, the trends in Figure 4c,f would be difficult to explain, as increased \(V_s\) doping would be expected to lower \(\mu\), contrary to observations.

To provide a fuller picture of the evolution of key transport parameters, Figure 5 plots the S:Fe loading dependence of \(d\rho/dT(300\, K)\), \(n(300\, K)\), \(\Delta E\), and \(\mu_{max}\) for both high-purity crystals (panels (a)–(d), left side, green points) and standard purity crystals (panels (e)–(h), right side, red points). To improve statistics, the data points shown here are average values from at least two to three crystals at each S:Fe loading, the error bars representing standard deviations. An equivalent plot showing values for each individual crystal can be found in the Supporting Information (Section C, Figure S4). Beginning with the behavior of \(d\rho/dT\), Figure 5a plots \(d\rho/dT\) vs. S:Fe loading (solid points for negative values, open points for positive values) for high-purity crystals. As the S:Fe loading is decreased, the large negative \(d\rho/dT\) systematically decreases in magnitude, inverting to positive \(d\rho/dT\) below a S:Fe loading of \(\sim 2.0\). Similar behavior is found in standard purity crystals (Figure 5e), albeit from lower initial negative \(d\rho/dT\), due to the additional impurity doping. These trends in \(d\rho/dT\) with S:Fe loading are interpreted in terms of increasing n-doping by \(V_s\) as the S:Fe loading during growth is decreased, driving the system toward phonon-limited transport and an IMT, as discussed further in Section 3.3.

Correlated with this behavior in \(d\rho/dT\), Figure 5b shows that the average \(n(300\, K)\) in high-purity crystals is constant at \(\sim 10^{16}\, cm^{-3}\) at high S:Fe loading (>2.2) but increases by an order of magnitude below this, reaching \(\sim 2 \times 10^{17}\, cm^{-3}\). At the lowest S:Fe loadings, \(n\) thus exceeds the \(\sim 1\, ppm\) (or \(8 \times 10^{16}\, cm^{-3}\)) concentration (Table 1) of Co, the only known shallow donor in these crystals, even at 300 K. The actual donor concentrations (from \(n(T \to \infty)\)) will thus safely exceed the Co concentrations. As an illustration, the application of eq 1, i.e., in the crude approximation of neglecting compensation, to \(n(T)\) data from high-purity crystals at a S:Fe loading of >2.3 results in \(N_A \approx 10^{19} - 10^{21}\, cm^{-3}\), exceeding the Co concentration by at least 2 orders of magnitude. This rules out explanations for the observed trends with S:Fe loading in terms of varying Co concentrations. The \(N_D\) of \(10^{19} - 10^{21}\, cm^{-3}\) even exceeds the total MBI concentration (by at least 1 order of magnitude), ruling out any observed impurity as the primary donor in these crystals. In addition, as noted in Section 3.1, the fact that \(n\) increases with decreasing S:Fe loading in Figure 5b is qualitatively at odds with any simple explanation based on total MBI concentration. The latter decreases with decreasing S:Fe loading (likely due to increased growth rate), in contrast with the observation of heavier doping at lower S:Fe loadings.
We thus contend that increased V\textsubscript{s} density at reduced S:Fe loading is the only simple interpretation of these data. As shown in Figure 5f, a similar trend in $n(300\text{ K})$ is observed in standard purity crystals but with larger overall values and lower dynamic range, due to additional impurity doping.

Figure 5c,g shows the S:Fe loading dependence of the activation energy, $\Delta E$, from $n(T)$. In high-purity crystals (Figure 5c), $\Delta E$ saturates at $\sim225$ meV at high S:Fe loading, in good agreement with recent reports on high-quality unintentionally doped FeS\textsubscript{2} crystals.$^9,10$ As the S:Fe loading is decreased below $\sim2.4$, however, $\Delta E$ decreases by over an order of magnitude, reaching 17 meV at a S:Fe loading of 1.69.

We interpret these data in terms of a deep donor state due to V\textsubscript{s}, located $\sim225$ meV below the conduction band minimum, as in Figure S5a (Supporting Information Section D). In the low V\textsubscript{s} density limit, at high S:Fe loading, where interdonor interactions are negligible, $\Delta E$ is thus $225$ meV. As the V\textsubscript{s} concentration increases when S:Fe loading is decreased, the individual donor states broaden into a donor band, increasing the Fermi energy, decreasing $\Delta E$, and approaching the $\Delta E \rightarrow 0$ limit expected at the IMT (where $d\rho/dT$ becomes positive).

The nature of this IMT is discussed further in Section 3.3.

A similar trend to Figure 5c is found for standard purity crystals (Figure 5g), albeit with a high S:Fe loading $\Delta E$ of...
~100 meV, significantly lower than high-purity crystals. As discussed in the Supporting Information (Section E), there are several possible explanations for this. One is that the additional MBI n-doping in standard purity crystals shifts the Fermi level during growth, modifying the enthalpy of formation of charged $V_S$ and thus the $V_S$ concentration at a given S vapor pressure. This would alter the correspondence between S:Fe loading and $V_S$ concentration, making direct comparisons between Figure 5c,g invalid. Another possibility is that the MBIs modify the energy of the $V_S$ states. Although this would require a ~100 meV shift (from ~225 to ~100 meV) with an MBI concentration of only ~500 ppm, this may be possible through the formation of defect complexes. Alternatively, Ni, the highest contributor to the MBI concentration in standard purity crystals, and the most likely to be an n-dopant (by balancing Ni$^{2+}$ formation with electron doping), could also be a deep donor in pyrite, generating states ~100 meV beneath the conduction band minimum (see the Supporting Information Section D, Figure S5b for a schematic). This could result in the saturation of $\Delta E$ at ~100 meV in Figure 5g, as discussed in the Supporting Information Section E, including Figure S6. Prior work on Ni substitution in FeS$_2$ is inconclusive, however, featuring $\rho(T)$ or $n(T)$ behavior that suggests increasing $\Delta E$ with Ni concentration, counter to expectations. While further work examining the impact of Ni in high-quality FeS$_2$ single crystals is clearly worthwhile, this uncertainty has no impact on the main conclusions here: $V_S$ are deep donors in pyrite, and their concentration can be systematically varied to tune n-doping over a wide range.

Figure 5d,h shows that in both purities of crystals, $\mu_{max}$ increases (up to ~1000 cm$^2$ V$^{-1}$ s$^{-1}$) as the S:Fe loading is decreased. As noted in the discussion of Figure 4, this is interpreted in terms of increased n-doping due to $V_S$ at low S:Fe loading, leading to the improved screening of scattering from a background of charged impurities (including compensating acceptors), leading to decreased ionized impurity scattering and improved mobility.

Finally, we comment briefly on the saturation of essentially all transport parameters plotted in Figure 5 in the high S:Fe loading limit. The simplest interpretation of such data is that $V_S$ concentrations have been suppressed to the lowest achievable levels in our CVT growth. As returned to below (Section 4), defect management to yet further suppress doping in this regime would ultimately be desirable in pyrite.

3.3. Electronic Transport: Nature of the Insulator–Metal Transition. The observation of phonon-limited bulk $\rho(T)$ and an approach to an IMT in heavily $V_C$-doped FeS$_2$ (e.g., Figure 3), albeit obscured from full view by surface conduction at low $T$, is worthy of further comment. IMTs in semiconductors doped with shallow donors/acceptors, such as Si:P, Si:B, Ge:As, or GaAs:Si, have been studied for decades. The IMT in semiconductors doped with deep donors/acceptors, however, is more challenging, both experimentally and theoretically. The spatial extent of donor wave functions, $a_d$, can be simply approximated as $a_d \approx \hbar/(2m^*E_D)^{1/2}$, where $m^*$ is the electron mass (0.45–0.49$m_e$), and $E_D$ is the donor energy. Energies up to 225 meV, as observed here, result in very low $a_d \approx 6 \AA$, far smaller than typical Bohr radii of shallow donors. Naive application of the Mott criterion for the critical density for the IMT, $n_i \approx (0.2/a_d)^2$, then yields high $n_i \approx 10^{18}$–$10^{20}$ cm$^{-3}$. Until relatively recently, such deep-donor-induced semiconductor IMTs had, in fact, not been achieved, as these concentrations often exceed equilibrium solubility limits. Progress with nonequilibrium processing using techniques like ion implantation, pulsed-laser melting, and rapid thermal treatment has changed this, however, realizing “hyperdoped” semiconductors. Si, for example, can be doped beyond equilibrium concentrations with deep (e.g., 250–480 meV) double donors S and Se, inducing an IMT. The IMT is understood to occur when interdonor interactions broaden the donor band to the point of overlap with the conduction band, pushing the Fermi energy above a mobility edge, as can be envisioned for FeS$_2$ with Figure S5a (Supporting Information).

In this context, results presented in this work potentially take on broader interest. If an IMT in pyrite can indeed be induced via doping with 225 meV deep donors due to $V_S$, this would constitute a unique case where such a transition is achieved with a native defect, incorporated during growth (as opposed to postgrowth nonequilibrium processing). This could potentially provide facile access to an important materials physics issue that is otherwise difficult to study. Detailed investigation of the IMT requires low $T$ transport measurements, however, which could only be achieved in pyrite FeS$_2$ through the successful mitigation of surface conduction or via some means to make direct contact with the bulk. This stands as a challenge in the field.

4. CONCLUSIONS

The above results provide compelling evidence that $V_S$ are deep donors in pyrite FeS$_2$ that they are responsible for unintentional doping of single crystals, and that they enable wide-range control over n-doping. As noted in the Introduction, however, theoretical studies have concluded (i) that $V_S$ may not be effective n-dopants and (ii) that they may have formation energies large enough to preclude equilibrium concentrations of ~10$^{20}$ cm$^{-3}$ at the current growth temperatures. With respect to (i), we emphasize that further DFT work on $V_S$ in FeS$_2$ is clearly warranted. Some of the current authors are in fact engaged in such a study, considering not only isolated $V_S$ but also $V_S$ clusters, which are possible in pyrite and could form donor states. Other $V_C$-containing defect complexes also warrant further study, as the results presented here cannot discount $V_S$ complexes vs isolated $V_S$. This is also important with respect to (ii), as $V_S$ clusters/complexes could have lower formation enthalpies than isolated $V_S$. Incorporation of $V_S$ during CVT growth of pyrite may also be controlled by a surface formation enthalpy lower than bulk (Δ$H_V$ below ~1 eV is required for the concentrations observed in this work) and could be a nonequilibrium incorporation process due to slow diffusion.

Such discussion highlights another important question, which is what is the results presented here imply for unintentionally doped pyrite films, which can have much larger electron densities than single crystals. Additional work to establish whether thin-film doping can also be explained by $V_S$, as suggested by the universal $\mu$–$n$ relation in crystals and films, is clearly needed. Ultimately, the control of n-doping in the manner shown here is also needed in thin films, and this work lays a foundation for such an effort. Another important point is that even in crystals, additional work to further reduce the density of $V_S$ and other defects in FeS$_2$ is desirable, in order to obtain lower electron densities. The $n$ values in this work, for example, still significantly exceed the intrinsic carrier density.
Nevertheless, the 300 K $n$ values below $10^{16}$ cm$^{-3}$ obtained in this work are in the range appropriate for solar cells, demonstrating, in agreement with other recent single-crystal work, that this is possible in pyrite. The mobilities obtained in this range are up to 100 cm$^2$ V$^{-1}$ s$^{-1}$, which should also be sufficient; this value could additionally be improved by the further reduction in background doping discussed above. Achieving all of this in thin films, where pyrite PV is most appealing, stands as a major challenge.

In summary, thoroughly characterized high-quality pyrite FeS$_2$ single crystals have been shown to exhibit increased bulk Hall electron density and mobility, decreased bulk resistivity, and approach to an insulator–metal transition when grown at progressively decreased S vapor pressure. These changes are uncorrelated with impurity concentrations and can only be simply interpreted in terms of a sulfur-vacancy-related deep ($\sim 225$ meV) donor. Wide-range and controlled n-doping of FeS$_2$ is thereby realized, simply by varying growth conditions. This work thus contributes substantially to the elucidation and control of doping in pyrite, a critical limiting factor in its development as a low-cost, earth-abundant, nontoxic photovoltaic material.

**REFERENCES**


(58) Yahia, J. Dependence of the Electrical Conductivity and
Thermoelectric Power of Pure and Aluminum-Doped Rutile on
1711–1719.

(59) Weihre, R. L. Electrical Properties of Single Crystals of Indium

(60) Fan, J. C. C.; Goodenough, J. B. X-Ray Photoemission

(61) Watson, E. B.; Cherniak, D. J.; Frank, E. A. Retention of
Biosignatures and Mass-Independent Fractionations in Pyrite: Self-

Kinetics and Mechanism of the Pyrite-to-Pyrrophite Transformation.

(63) Butler, S. R.; Bouchard, R. J. Single Crystal Growth of Pyrite

(64) Brostigen, G.; Kjekshus, A. Redetermined Crystal Structure of

(65) Fleet, M. E. The Crystal Structure of a Pyrrhotite (Fe7S8). *Acta
1867.

(66) Fiechter, S.; Mai, J.; Ennaoui, A.; Szacki, W. Chemical Vapour
Transport of Pyrite (FeS2) with Halogen (Cl, Br, I). *J. Cryst. Growth*
1986, 78, 438–444.

(67) Brandon, D.; Kaplan, W. D. Microstructural Characterization of

(68) Maxwell, J. A.; Campbell, J. L.; Teesdale, W. J. The Guelph

(69) Bither, T. A.; Bouchard, R. J.; Cloud, W. H.; Dokohue, P. C.;
Siemons, W. J. Transition Metal Pyrite Dichalcogenides. High-
1968, 7, 2208–2220.

(70) Bayliss, P. Crystal Structure Refinement of a Weakly

(71) Blenk, O.; Bucher, E.; Willeke, G. p-Type Conduction in Pyrite

(72) Voigt, B.; Moore, W.; Walter, J.; Manno, M.; Aydil, E. S.;
Leighton, C. unpublished.

(73) Ashcroft, N. W.; Mermin, N. D. *Solid State Physics*; Harcourt
College, 1976.

(74) Sze, S. M. *Physics of Semiconductor Devices*; John Wiley & Sons:
New York, 1981.

(75) Ho, C. H.; Huang, C. E.; Wu, C. C. Preparation and

(76) Mott, N. F. *Metal-Insulator Transitions*, 2nd ed.; Taylor &
Francis, 1990.

(77) Shklovskii, B. I.; Efros, A. L. *Electronic Properties of Doped

(78) Karguppikar, A. M.; Vedeshwar, A. G. Transport Properties of

40, 677–683.


(81) Winkler, M. T.; Recht, D.; Sher, M.; Said, A. J.; Mazur, E.; Aziz, M. J.

(82) Younkin, R.; Carey, J. E.; Mazur, E.; Levinson, J. A.; Friend, C.
M. Infrared Absorption by Conical Silicon Microstructures Made in a
Variety of Background Gases Using Femtosecond-Laser Pulses. *J.

(83) Crouch, C. H.; Carey, J. E.; Shen, M.; Mazur, E.; Génin, F. Y.
Infrared Absorption by Sulfur-Doped Silicon Formed by Femto-