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Synthesis, Characterization and Fabrication of Ultrathin Iron Pyrite (FeS$_2$) Thin Films and Field-effect Transistors

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We reported a synthesis of an ultrathin FeS$_2$ thin film via thermal sulfurization of an iron thin film and its fabrication process for field-effect transistors. Reaction time was found to be essential for the growth of the crystallized FeS$_2$ thin film. The thickness of Fe increased from 10nm to 35nm after the reaction. The FeS$_2$ thin film has a resistivity of 0.345 Ω·cm and a Hall mobility of 7.1 cm$^2$ V$^{-1}$ s$^{-1}$, with a carrier concentration of 2.89×10$^{17}$ cm$^{-3}$. The fabricated FeS$_2$ transistors have a reported highest current on/off ratio of 3.94×10$^5$ and Ion of 0.117 mA. Moreover, the FeS$_2$ based transistor not only broader the applications of pyrite, but also provides a platform for investigation of FeS$_2$ materials. Temperature-dependent electrical transport measurements confirmed the rich intrinsic defect states in the FeS$_2$ thin film, which indicates that reducing intrinsic defect might be the key issue to further improve the device performance.

Introduction

Iron pyrite (FeS$_2$), which is also known as fool’s gold, is an intriguing semiconductor that is an abundant mineral in the Earth. It is widely found in quartz veins, sedimentary rocks and coal beds, and it has attracted continuous interest since the 1970s because it is a rich resource and has unique properties. FeS$_2$ has a small band gap (0.8-0.95 eV) and a large light absorption coefficient ($\alpha = 6 \times 10^5$ cm$^{-1}$, $h\nu > 1.3$ eV), making it a promising candidate for solar energy conversion. The highest reported electron carrier mobility is approximately 360 cm$^2$ V$^{-1}$ s$^{-1}$, with a minority carrier diffusion length of 0.1-1 μm. These properties make FeS$_2$ a potential alternative thin layer absorber for photovoltaic (PV) and photo-electrochemical solar cells.

However, despite all the excellent properties of pyrite, the best pyrite-based solar cell only has an energy conversion efficiency of 3%. Researchers have experienced difficulties in improving its performance, primarily because of the low fill factor (approximately 0.5) and open circuit voltage (≤ 200 mV) caused by the high recombination loss and the rich density of the sulfur defect states. Additionally, the doping mechanism and method of FeS$_2$ materials is not clear.. These disadvantages prevent FeS$_2$ from creating a p-n homojunction or a p-i-n junction in solar cells. With the emergence of other promising materials for thin film solar cells, including CuInGaSe$_2$, the potential of FeS$_2$ as a candidate for solar PV applications has waned. Recently, FeS$_2$ has attracted interest once again because of its low cost and potential applications for field-effect transistors (FETs). Several new synthesis methods have been described to improve the FeS$_2$ thin film quality and properties, such as chemical vapor deposition (CVD), the sulfidation of FeO$_3$, molecular beam epitaxy (MBE), sputtering, sol-gel, and electrodeposition. Moreover, substantial effort has been focused on the low-cost colloidal synthesis of pyrite nanocrystals. Different pyrite morphologies, such as nanowires, nanobelts and nanoplanes, have also been synthesized and reported. These synthetic improvements have led to broader applications besides PV and Photo-electrochemical solar cell. For instance, Qihua Xiong et al. used FeS$_2$ thin film as counter electrodes for Dye-Sensitized Solar Cells (DSSC) utilizing I$_3^-$/I$^-$ and Co(III)/Co(II) as the electrolyte. The new (DSSC) gives a photoconversion efficiency around 8% which is comparable to Pt. Song Jin et al. utilized FeS$_2$ nanowires as cathodes materials in Li-ion battery using a liquid electrolyte, which retains a discharge energy density of 534 Wh kg$^{-1}$ at 0.1C rate while has a discharge capacity of 350mAh g$^{-1}$. Other potential usage including hole transportation, photodetector, and even in agriculture. FeS$_2$ is earth abundant and low cost materials. Hence the development in FeS$_2$ application will benefit many different fields and further lower the cost for industry.

However, although FeS$_2$ has a very unique electrical properties, its potential usage in FETs has not yet been fully developed. Figure 1 shows the computational band structure of FeS$_2$. For instance, Qihua Xiong et al. used FeS$_2$ thin film as counter electrodes for Dye-Sensitized Solar Cells (DSSC) utilizing I$_3^-$/I$^-$ and Co(III)/Co(II) as the electrolyte. The new (DSSC) gives a photoconversion efficiency around 8% which is comparable to Pt. Song Jin et al. utilized FeS$_2$ nanowires as cathodes materials in Li-ion battery using a liquid electrolyte, which retains a discharge energy density of 534 Wh kg$^{-1}$ at 0.1C rate while has a discharge capacity of 350mAh g$^{-1}$. Other potential usage including hole transportation, photodetector, and even in agriculture. FeS$_2$ is earth abundant and low cost materials. Hence the development in FeS$_2$ application will benefit many different fields and further lower the cost for industry.
 compared with those of other transition-metal dichalcogenides (TMDs) and commonly used semiconductors. The band gap of FeS$_2$ is slightly smaller than that of silicon (1.1 eV), which makes it a natural alternative material for electrical devices. Other TMD materials, including MoS$_2$ (~1.29 eV) and WS$_2$ (~1.4 eV), usually have larger band gaps. Although there have been a few research reports addressing FeS$_2$ FET devices, the performance of these devices remains far from satisfactory. For example, although a recently reported FeS$_2$ nanowire FET device has a mobility of approximately 0.1-0.2 cm$^2$ V$^{-1}$ s$^{-1}$ at a carrier concentration of approximately 2.9×10$^{14}$ cm$^{-3}$, it is difficult to pinch off, which leads to a low $I_{on}/I_{off}$ ratio for the output current. Some of the reported FeS$_2$ thin film materials electrical properties is listed in Table 1 and compared with our work. A further understanding of the electrical transportation for materials and device is needed to further improve the performance of FeS$_2$.

![Figure 1. Absolute band edge positions of the selected materials](image1)

**Table 1. Reported FeS$_2$ materials electrical properties**

<table>
<thead>
<tr>
<th>Mobility (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
<th>Carrier Concentration (cm$^{-3}$)</th>
<th>Thickness (nm)</th>
<th>Resistivity (Ω cm)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.450</td>
<td>7.69×10$^{10}$</td>
<td>90±10</td>
<td>0.5605</td>
<td>24</td>
</tr>
<tr>
<td>0.271</td>
<td>2.1×10$^{10}$</td>
<td>70</td>
<td>0.11</td>
<td>24</td>
</tr>
<tr>
<td>11.8</td>
<td>2.5×10$^{13}$</td>
<td>400</td>
<td>0.58</td>
<td>35</td>
</tr>
<tr>
<td>2.12</td>
<td>4.90×10$^{18}$</td>
<td>200±50</td>
<td>0.58</td>
<td>25</td>
</tr>
<tr>
<td>7.1</td>
<td>2.89×10$^{18}$</td>
<td>35</td>
<td>0.345</td>
<td>This work</td>
</tr>
</tbody>
</table>

In order to develop the application for FeS$_2$ based FET, we studied the growth of FeS$_2$ and improve the quality of the FeS$_2$ thin film. We investigated the simplest synthesis among with the methods mentioned above: ex-situ thermal sulfidation of an Fe thin film as Figure 2. We synthesized a very thin films under atmospheric pressure using an iron target. The FeS$_2$ layer was approximately 300 nm and was deposited by low pressure chemical vapor deposition (LPCVD). The film was then placed in a custom-designed chemical vapor deposition furnace system on a quartz boat. The furnace setup is shown in Figure 2, the sulfur was placed upstream, and the film was placed downstream. The sulfur was heated by a silicone rubber heat belt and controlled by a digital temperature controller. At 160 °C, the sulfur existed in both the liquid and gas phases. The mixture was sent into the furnace with argon at a rate of 200 sccm. The sulfurification temperature was held constant at 500 °C with a ramping speed of 10 °C per min, as reported by other studies. We used reaction times of 180, 240 and 360 min, and the sulfur flow was stopped immediately after the reaction.

**Figure 1. Absolute band edge positions of the selected materials**

**Experiment Section**

### FeS$_2$ Thin Film Fabrication

The FeS$_2$ thin film was synthesized via two commonly used two-step ex-sulfurization processes. First, we deposited 10 nm of an Fe thin film on a pre-prepared SiO$_2$/Si substrate using D.C. magnetron sputtering with an iron target. The SiO$_2$ layer was approximately 300 nm and was deposited by low pressure chemical vapor deposition. The film was then placed in a custom-designed chemical vapor deposition furnace system on a quartz boat. The furnace setup is shown in Figure 2, the sulfur was placed upstream, and the film was placed downstream. The sulfur was heated by a silicone rubber heat belt and controlled by a digital temperature controller. At 160 °C, the sulfur existed in both the liquid and gas phases. The mixture was sent into the furnace with argon at a rate of 200 sccm. The sulfurification temperature was held constant at 500 °C with a ramping speed of 10 °C per min, as reported by other studies. We used reaction times of 180, 240 and 360 min, and the sulfur flow was stopped immediately after the reaction.
reaction by removing the heat belt. After the sulfurization process, the system cooled to room temperature at the natural cooling rate. The same method is also used on quartz substrate with reaction time for 240 min for optical properties characterization.

FeS$_2$ FET Fabrication

The as-synthesized FeS$_2$ thin film was first cleaned using four cycles of deionized (DI) water and then dry-etched with an induced coupled plasma (ICP) etcher after a photolithography process. After dry etching, the drain and source electrodes were defined by a second photolithography process, and then, Ni (200 Å)/Ti (700 Å)/Au (300 Å) stack layers were deposited via e-beam evaporation as the source/drain metal. Acetone and isopropanol were used for the lift-off process, and the device was cleaned with DI water.

Characterization

The thin film X-ray diffraction (TFXRD) pattern of the as-synthesized sample was collected on an Empyrean (PAN analytical) Diffractometer using Cu Kα radiation. The tube current and tube tension were 40 mA and 40 kV, respectively. The data were collected from 20 degrees to 60 degrees with a measurement time of 1 second and 0.06 degrees per step. Raman spectra of the as-synthesized sample were collected on an InVia (Renishaw) confocal microscope using an Ar ion laser (514.5 nm and 50 mW). The resistivity, Hall mobility and carrier concentration were measured using a Keithley 2182A nanovoltmeter and a 6221 ac/dc source.

Results and Discussion

X-ray diffraction is the primary technique to determine the phase and quality of a thin film. Because of the small thickness, thin film X-ray diffraction (TFXRD) was used in our experiments. The XRD pattern of the as-synthesized FeS$_2$ thin film is plotted in Figure 3, including the 180-, 240- and 360-min samples. All the peaks can be indexed to pyrite (JCPDS no. 00-026-0801), marcasite (JCPDS no.00-003-0795) and silicon (JCPDS no. 00-003-0544). Increasing the sulfurization time to 240 min causes a blue shift of the peaks from 338 to 339 cm$^{-1}$, from 372 to 374 cm$^{-1}$ and 424 to 427 cm$^{-1}$. The peak further blue shift to 341 cm$^{-1}$, 374 cm$^{-1}$ and 427 cm$^{-1}$ respectively when the reaction time increase to 360 min. It also generated of a marcasite peak at approximately 320 cm$^{-1}$, which agrees with the TFXRD result. We attribute the blue shift to a strong interaction between the S-S and Fe-S bonds because of the longer annealing time.$^{9,29,40}$

To further investigate the FeS$_2$ phase, confocal micro-Raman spectroscopy was used. It has been shown that Raman spectroscopy is more sensitive to different phases of FeS$_2$, and it is widely used in characterization. The Raman spectrum in Figure 4 for the 180-min sample shows three peaks at 338 (S$_2$ liberation, $E_g$), 372 (S−S in-phase stretch, $A_g$) and 424 cm$^{-1}$ (coupled libration and stretch, $T_{g(3)}$) that belong to pyrite.$^{10,13,38}$ Increasing the sulfurization time to 240 min causes a blue shift of the peaks from 338 to 339 cm$^{-1}$, from 372 to 374 cm$^{-1}$ and 424 to 427 cm$^{-1}$. The peak further blue shift to 341,376 and 427 cm$^{-1}$ respectively when the reaction time increase to 360 min. It also generated of a marcasite peak at approximately 320 cm$^{-1}$, which agrees with the TFXRD result. We attribute the blue shift to a strong interaction between the S-S and Fe-S bonds because of the longer annealing time.$^{9,29,40}$

AFM is a useful technique to study the morphology of thin films. In Figure 5, the reaction time can be seen to have a critical impact on the thin film surface. For the reaction time of
180 min shown in Figure 5a, the sample surface is extremely uneven with a surface roughness of approximately 17.47 nm. This sample is likely in the process of crystallization, and hence, the quality of the sample is poor. The grain size is average of 50 gains in the AFM image.

The optical property of the FeS$_2$ thin film of our synthesis is also investigated. We grew FeS$_2$ thin film on quartz substrate. Raman spectrum showed the FeS$_2$ has very good quality in Figure S1. Detail of the optical property can be seen in Figure S2.

The electrical properties of the FeS$_2$ thin film were studied and are shown in Figure 7. The 240-min sample shows superior properties compared with the 180- and 360-min samples, primarily because of the improved crystallization, its mobility and carrier concentration are suitable for FETs. The values recorded for these properties are about $2.9 \times 10^{18}$ cm$^{-3}$ and 7.13 cm$^{-2}$ V$^{-1}$ s$^{-1}$, respectively, which are relatively high compared with other reports. Although the 360-min sample shows some discontinuity, it maintains a high conductivity because of the larger grain size.

Based on the electrical properties of the FeS$_2$ thin film, we fabricated FeS$_2$ FETs using the 240 min sample, as mentioned in the experimental section. A schematic and an optical microscope image of the FET are shown in Figure 8a. There is a narrow edge (green edge and circled out) around the FET device, which will be discussed in detail later. Additionally, the cracks at the surface were generated by the device fabrication process. The thin film may have folded due to the stress, thus creating cracks. The thickness of the FeS$_2$ thin film is approximately 35 nm, as measured by a profilometer, which is 3.5 times that of the iron thin film precursor deposited by e-beam evaporation. The expansion factor is consistent with other reported results. The transfer curve ($I_{ds}$ vs. $V_{gs}$) and output curve ($I_{ds}$ vs. $V_{ds}$) are shown in Figures 8b and 8c, respectively. The device edge is also clearly shown in the insert image of Figure 8b. An $I_{ds}/I_{off}$ ratio of 3.94$\times 10^{4}$ was obtained, which is larger than for any other FeS$_2$ FET devices reported. Two steps are needed to increase the $I_{ds}$ in the transfer curve. The first step, which has an $I_{ds}/I_{off}$ ratio of approximately 10$^{4}$, is caused by the edge effect caused by the thin slice mentioned above. Although increasing the $V_{gs}$ will overcome the edge effect, the device will fully turn on at approximately $V_{gs} = -25$ V. Although the change is small, the $I_{ds}$-$V_{ds}$ in Figure 8c shows that the active channel of the device can be modulated by the gate.

**Figure 5.** AFM images of different samples

XPS was then used to determine the elemental composition of the FeS$_2$ thin film surface. The XPS spectra of the 240-min sample are shown in Figure 6a. The peak at a binding energy of 162.4 eV is attributed to intrinsic bulk-like disulfides (BD) and belongs to S 2p$_{3/2}$. S 2p$_{3/2}$ has a peak at 163.5 eV, which is also characteristic of FeS$_2$. Additionally, a small shoulder at 161.3 eV is attributed to surface disulfides (NSD and SD) on the (100) surface of iron pyrite caused by sulfur vacancies. The peak at 164.8 eV is often described as high energy, and it is caused by a core hole effect, as discussed in recent papers. All the results show that the FeS$_2$ thin film surface contains many sulfur defects, which will be discussed later in the paper. Figure 6b reveals the binding energies of the Fe 2p. The peaks at 707.1 eV and 719.8 eV belong to Fe-S 2p$_{3/2}$ and Fe 2p$_{1/2}$, respectively. The small peak at approximately 711 eV is attributed to Fe-O and is the result of exposure to air.

**Figure 6.** XPS spectra of the 240-min FeS$_2$ sample

The electrical properties of different samples of FeS$_2$. The first step, which has an $I_{ds}/I_{off}$ ratio of approximately 10$^{4}$, is caused by the edge effect caused by the thin slice mentioned above. Although increasing the $V_{gs}$ will overcome the edge effect, the device will fully turn on at approximately $V_{gs} = -25$ V. Although the change is small, the $I_{ds}$-$V_{ds}$ in Figure 8c shows that the active channel of the device can be modulated by the gate.
High-k dielectric materials, including Al$_2$O$_3$ and ZrO$_2$, may increase the device mobility and enhance its performance.\(^{45}\) To test the electrical contact used in the device, Figure 8d shows the transmission line method (TLM) test of the FeS$_2$ devices. The linear slope shows the ohmic contact for the FeS$_2$ thin film. According to the slope, the device has a sheet resistance of approximately 3467 $\Omega$/sq, and the sheet resistance observed via the TLM is smaller than recorded using the Resistivity/Hall system, which may be due to the low contact resistance of the metal contact. Instead of pristine silver paste, a stack layer of Ti/Ni/Au was deposited by E-beam evaporation with the thickness 10nm/90nm/20nm. Here, the thin Ti layer was used as the glue layer to improve the contact of the metal electrode with the FeS$_2$ thin film. The layer of gold was used to reduce the contact resistance between the probes and the metal pads of devices during the measurement. Thus, the metal exhibited a low series resistance of approximately 1827 $\Omega$, which is shown at the plot intercept in Figure 8d.\(^{46}\)

Although the $I_{on}/I_{off}$ ratio is much higher than previous reported FeS$_2$ transistor, it is still low for further application in electronics area. In order to reveal the problem that cause the low $I_{on}/I_{off}$ ratio, we studied the electrical transport mechanisms of the FeS$_2$ thin film using a temperature-dependent four probe electrical measurement. Figure 9a shows the $I_{on}$-$V_{ds}$ curves at different temperatures. The resistance of the active channel increased as the temperature decreased. The conductivity was calculated using the parameters of the FeS$_2$ device. Figure 9b is plotted as $\ln(\sigma)$ versus $T^{1/4}$, and we obtained a linear relationship for low temperature. This finding indicates that the conductivity follows the Mott VRH mechanism:\(^{47}\)

$$\sigma = \sigma_0 \exp\left(-\frac{T}{T_0}\right)^{1/4},$$

where $\sigma_0$ is the prefactor and $T_0$ is the Mott VRH temperature.\(^{48}\) This mechanism indicates that the electron is hopping among localized states in the disordered system.\(^{49,50}\) In the FeS$_2$ thin film, the disorder is attributed to the random distribution of defects and impurities that results in the localization of charge carriers.\(^{48,51}\) As we discussed in the XPS section, the FeS$_2$ thin film is a defect-rich system. Combined with the FET transport behaviour, these results suggest that the electrical transport is primarily influenced by localized defects in the crystalline FeS$_2$ thin film.

### Table 2. Parameters of the FeS$_2$ FET device

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
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</thead>
<tbody>
<tr>
<td>W/L</td>
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<td>$\mu$m</td>
</tr>
<tr>
<td>Gate dielectric layer thickness</td>
<td>300</td>
<td>nm</td>
</tr>
<tr>
<td>$Cox$</td>
<td>1.15E-04</td>
<td>$F/m^2$</td>
</tr>
<tr>
<td>On-State Resistance</td>
<td>4.38E5</td>
<td>$\Omega$</td>
</tr>
<tr>
<td>Off Current</td>
<td>2.97E-9</td>
<td>$A$</td>
</tr>
<tr>
<td>On Current</td>
<td>1.17E-4</td>
<td>$A$</td>
</tr>
<tr>
<td>$V_{th}$</td>
<td>-25</td>
<td>$V$</td>
</tr>
<tr>
<td>Device Mobility</td>
<td>0.223</td>
<td>$cm^2/V^0.5$</td>
</tr>
<tr>
<td>$\rho$</td>
<td>0.256</td>
<td>$\mu S$</td>
</tr>
<tr>
<td>Carrier Concentration</td>
<td>2.94E19</td>
<td>cm$^{-3}$</td>
</tr>
</tbody>
</table>

### Figure 9. Temperature dependence of the FeS$_2$ samples

**Conclusion**

We demonstrated a successful method for synthesizing an ultrathin FeS$_2$ thin film via thermal sulfidation of an iron thin film. The phase of the FeS$_2$ thin film was confirmed using TFXRD and Raman spectroscopy. Although a small amount of marcasite is present, the FeS$_2$ thin film obtained using 240 min
of sulfidation exhibits the best electrical properties, including resistivity, mobility and carrier concentration, for FET applications. Given the quality of the FeS$_2$ thin film, we fabricated a FET device with an $I_{ON}/I_{OFF}$ ratio of approximately $4 \times 10^4$. Although the device is relatively difficult to control with the gate voltage, the potential for the use of FeS$_2$ in FET applications was demonstrated. The electron transport mechanism was also studied using temperature-dependent electrical transport measurements. The methodology used to generate the thin film and FET device provides a versatile platform to further improve the quality of FeS$_2$ thin films as promising candidates in FET materials.

We found that our polycrystalline film has many surface defects and grain boundaries, which sharply reduce the material’s quality and device performance. These are also an issue for FeS$_2$ photovoltaic solar cells. A high density surface state will cause high recombination, which limits the conversion efficiency. The low mobility of the FET device is the main challenge limiting the utility of FeS$_2$. To enhance the mobility of the device, we believe that a high $k$-dielectric gate layer and an effective passivation layer are the solution.$^{34,45}$ High $k$-dielectric materials reduce the gate layer thickness and increase the control ability of the gate voltage, whereas the passivation layer can reduce the surface defect states. Both methods could further enhance the channel modulation capability of FeS$_2$ devices.

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**Reference**


