Iron pyrite thin films deposited via non-vacuum direct coating of iron-salt/ethanol-based precursor solutions†

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We report a new approach for fabricating pyrite (cubic FeS₂) thin films via a non-vacuum direct solution coating route using iron-acetate dissolved in ethanol as a precursor solution. The precursor ink is deposited by spin coating and annealed in air at 300 °C to produce amorphous iron oxide films. Subsequent heat treatment of the iron oxide films in a sulfur environment at 450 °C results in the formation of phase-pure, carbon-free, large-grained pyrite films. In particular, the phase evolution during sulfuration is systematically investigated, focusing on the effects of the principal experimental variables such as temperature and pressure. As the temperature increases, iron oxide first begins to transform into marcasite (orthorhombic FeS₂) and then is completely converted to pyrite. Further increasing the temperature above 500 °C induces the decomposition of pyrite into pyrrhotite (Fe₇S₈) and sulfur vapor. The decomposition is also strongly dependent on the partial pressure of sulfur: as the pressure decreases, the decomposition occurs at lower temperature. The synthesized single-phase pyrite films show an indirect band gap of 0.94 eV, a strong anodic photocurrent based on photo-electrochemical measurements, and n-type semiconducting properties based on Mott–Schottky analysis. Thus, the films demonstrate great potential for use as absorbing layers in solar cells.

Introduction

Iron pyrite (cubic FeS₂) is gaining renewed interest as a low-cost, light-absorbing material for thin-film photovoltaics due to its abundance in the earth and non-toxicity. This surge of interest is also partly based on the recent significant reduction in the price of crystalline silicon solar cells, which has focused attention on cost-competitive thin-film absorption materials as alternatives to conventional materials containing rare-earth elements, such as CuInGaSe₂ (CIGS) and CdTe. In addition to its potential for cost reduction, iron pyrite is known to possess optoelectronic properties suitable for solar energy conversion, including a band gap of approximately 0.95 eV, a strong light absorption coefficient (α > 10⁵ cm⁻¹ for λ ≈ 700 nm), and long carrier drift and diffusion lengths.¹⁻³ Several promising device results, such as a large short-circuit photocurrent density (>30 mA cm⁻²) and a quantum efficiency over 90% in photo-electrochemical and solid-state Schottky solar cells based on pyrite single crystals, were demonstrated as far back as decades ago.²,⁶

A variety of thin-film deposition methods have been employed to form iron pyrite thin films, including chemical vapor deposition (CVD)⁷⁻⁹ and solution-based methods.⁵,¹⁰⁻¹⁵ Considering their production cost and scalability, non-vacuum, solution-based methods are preferable to vacuum-based technologies. Recent advances in solution-based CIGS thin film solar cells clearly demonstrate that the solution-based process is very attractive not only due to its low-cost potential but also due to its potential to produce high-performance devices. For example, in spite of the complexity of the CIGS material system, which consists of at least 4 elements, it has already been proven that device efficiencies greater than 15% can be achieved by these routes.¹⁶,¹⁷ With respect to CIGS thin film solar cells, the fabrication of iron pyrite via a solution-based route certainly represents the best material selection and process combination for producing thin-film solar cells with maximum cost effectiveness.

Non-vacuum, solution-based processes for fabricating inorganic semiconductor thin films are typically divided into two categories depending on the precursor type used: the first approach uses true solution precursors,⁵,¹⁰,¹¹,¹⁶,¹⁸ and the other uses particulate precursors.¹²⁻¹⁵,¹⁷,¹⁹⁻²¹ The potential of the direct
solution coating approach, which is also called the molecular ink approach, is a more cost-effective method than the particle-based one because a precursor solution with the appropriate rheology can be directly coated on a substrate without the need to pre-fabricate, purify, assemble, and passivate precursor nanoparticles.

Various combinations of precursor chemicals, solvents, and organic additives have been suggested and tested as inks for direct coating, including the following:

- Precursor chemicals: inorganic metal salts (nitrates and chlorides), carbon-containing metal salts (acetates and acetylacetone), metal chalcogenides, etc.
- Solvents: water, methanol, ethanol, pyridine, 2-methoxy-ethanol, hydrazine, etc.
- Organic additives: chelating agents, surfactants, binders, etc.

Despite the great flexibility allowed in designing precursor inks using the constituents listed above, the choice of the combination should meet the following criteria:

1. Low-toxicity and environmental friendliness.
2. Processability in ambient air throughout the entire process, including during solution preparation and film deposition.
3. Any carbon-containing constituents in the inks should exhibit facile thermal decomposition characteristics that are amenable to air drying.

The last criterion is extremely important because if the decomposition of carbonaceous materials is not properly optimized during the air-drying step, carbon residues can easily persist even after high-temperature post-annealing, which could generate detrimental effects on the film quality and device performance in various ways. Limited crystal growth, poor adhesion between deposited films and the corresponding substrates, and an increase in the series resistance of the final devices are typical drawbacks caused by residual carbon materials.

Among the suggested precursor chemical/solvent/organic additive combinations, the most attractive one satisfying all of the requirements outlined above is believed to be a metal acetate/ethanol/ethanolamine-type precursor solution because it has successfully produced nearly carbon-free Cl(G)S films with device efficiencies of up to 8% while featuring constituent chemicals that are cheap, less-toxic, easy to handle, and air-stable. The low sensitivity of metal acetates to moisture, their reduced susceptibility to precipitation due to the stable metal acetate/ethanolamine chelate complex, and the low dissociation energy of the ethanolamine structure may be the reasons for the promising results observed to date. These considerations motivated us to fabricate iron pyrite films using a similar combination of iron acetate/ethanol/(mono) ethanolamine.

In addition to the issues regarding the cost effectiveness of the fabrication process and carbon-free characteristics of the final films, the phase purity of the absorbing film is also a prerequisite for fabricating efficient photovoltaic devices because the different phases of iron sulfide have very different optoelectronic properties, most of which are metallic or semimetallic rather than semiconducting. Phase impurity has been considered to be one of the main reasons for the lack of progress in increasing the device efficiency of iron pyrite solar cells beyond 3% reported in 1991. Therefore, it is important to understand the phase evolution of the iron–sulfur system as a function of process parameters such as temperature and pressure to extract a suitable process window for obtaining single-phase pyrite with high reproducibility. However, there is only a limited number of papers reporting the phase evolution behavior of pyrite films, in particular, those derived via direct solution coating routes. Recently, Seefeld et al. reported that single-phase iron pyrite films can be synthesized from an Fe(acac)₃ molecular ink using pyridine as a solvent. However, such films were fabricated only after the precursor films (iron oxide) were subjected to a successive two-step sulfurization procedure in which the precursor films were first annealed in H₂S gas at 390 °C for 12 h and then annealed again in S vapor at 500 °C for 4 h. Thus, further study is needed to develop a more facile method for producing single-phase pyrite films with a single annealing step with shorter reaction time based on a more firm understanding of the phase evolution behavior that arises via this route.

In this work, we report that single-phase pyrite thin films can be fabricated by a simple direct solution coating route using an iron acetate/ethanol/monoethanolamine precursor solution. The amorphous iron oxide precursor films are completely converted to large-grained, carbon-free, single-phase pyrite after sulfurizing the precursor films in sulfur vapor at 450 °C for 30 min. A detailed phase evolution study reveals that iron oxide is first converted to marcasite at low temperature (<350 °C) and then transformed into pyrite at approximately 450 °C. A further increase in temperature induces the decomposition of pyrite into pyrrhotite and sulfur vapor, and this decomposition behavior is also strongly affected by the partial pressure of sulfur during sulfurization. Interestingly, the single-phase pyrite thin films fabricated via this route are observed to be n-type semiconductors with a very high doping density, as indicated by an electrochemical Mott–Schottky analysis, in contrast to most reports on pyrite thin films, which suggest that synthetic pyrite films are weakly p-type. Furthermore, the strong photo-electrochemical response of the fabricated films demonstrates their high potential to serve as absorbing layers for solar-cell applications.

Experimental section
Preparation of precursor solution
Iron(II) acetate (C₄H₆FeO₄ ≥99.99%), sulfur powder (≥99.98%), and MEA (≥99.0%) were purchased from Sigma-Aldrich. Ethanol (C₂H₅OH; ≥99.6%) was acquired from Junsei Chemical. All chemicals were used as received. Approximately 0.53 mol of iron acetate was dissolved in 26 mL of ethanol in a glass bottle, and 3 mL of MEA was then added to this solution to obtain a suitable viscosity for spin-coating.
Thin-film deposition

The precursor solution was coated on bare soda-lime glass or 1 µm thick Mo-coated SLG glass substrates by spin-coating (ACE-200, Dong-Ah Tech., Korea) at 2200 rpm for 20 s, after which the solution was immediately dried at 300 °C for 10 min in air on a hotplate to evaporate the solvent and induce the thermal decomposition of MEA. The thickness of the precursor film was controlled by varying the number of spin-coating and drying steps. The solution preparation and film deposition procedures were performed entirely in ambient air.

Sulfurization

Sulfurization was carried out in a heat-treatment chamber in which a graphite container was placed inside. The chamber was equipped with a temperature and pressure controller. The precursor samples were placed inside the graphite container along with 0.3 g of sulfur powder. The container was, then, covered with a graphite lid in a way that the lid simply rested on the container. After loading the samples in this way, the chamber was initially evacuated to a base pressure of 10⁻³ Torr with a rotary pump and then the background pressure was regulated by the injection of nitrogen gas. The effects of the main sulfurization parameters such as temperature (250 to 300 °C) and background pressure at room temperature (10⁻³ and 760 Torr) were investigated. It should be noted that our sulfurization chamber was designed to operate at a maximum pressure of 760 Torr using a pressure relief valve: the pressure during sulfurization was not allowed to exceed 760 Torr because beyond this point the door seal might leak.

Device fabrication

An iron pyrite heterojunction device was fabricated according to the structures of ITO/ZnO/Cds/FeSₓ/MoOᵧ/Al and Al/FeSₓ/Al. A ZnO thin film was deposited by radio-frequency (rf) magnetron sputtering on an ITO glass substrate, and a Cds layer was deposited by chemical bath deposition (CBD). After the formation of the pyrite film, the MoOₓ layer and the top Al electrode were deposited by using the thermal vaporization process.

Characterization

The morphology and composition of the precursor and sulfurized films were analyzed by high-resolution scanning electron microscopy (HRSEM, XL30SFE Phillips Co., Holland at 10 kV) and energy dispersive spectroscopy (EDS, EDAX Genesis apex, acceleration voltage: 30 kV, collection time: 100 s via a standard-less method), respectively. A compositional depth profile was obtained by Auger electron spectroscopy (AES, Perkin Elmer, SAM 4300).

Crystalline structures were characterized by X-ray diffraction (XRD) using a CuKα radiation source (λ = 1.5406 Å) and Raman spectroscopy. The Raman spectra were obtained in the quasi-backscattering geometry by using the 514.5 nm line of an Ar-ion laser as the excitation source. The scattered light was filtered through a holographic edge filter, dispersed using a Spex 0.55-m spectrometer, and detected with a liquid-nitrogen-cooled back-illuminated charge-coupled-device (CCD) detector array.

The optical transmittance was measured to estimate the optical band gap using a UV spectrophotometer (Shimadzu Japan, UV-vis-NIR 3101) over the wavelength range of 200 nm to 2600 nm, using a bare SLG substrate as a reference. Electrochemical and photoelectrochemical measurements were performed to further investigate the electrical and optical properties of the synthesized pyrite thin films. A conventional three-electrode cell contained in a 1 L multi-neck flask with a quartz window as a photon inlet was used. Pyrite films formed on Mo/SLG substrates were used as working electrodes. A platinum counter electrode and a saturated calomel electrode (SCE) positioned in a salt bridge with a silica tip were adopted in the cell. All electrode potentials in this work are referenced to the SCE. All electrochemical experiments were carried out at ambient temperature in deaerated pH 6.5 buffer solution. For photocurrent measurements, AM1.5G light produced from a class AAA solar simulator (WACOM, Japan) illuminated the pyrite films immersed in the deaerated pH 6.5 buffer solutions through the quartz inlet. Mott-Schottky plots were obtained to determine the dominant charge carrier type of the pyrite films by controlling the frequency response analyzer (FRA) at a fixed frequency of 100 Hz using an excitation voltage of 10 mV (peak-to-peak) at a scan rate of 1 mV s⁻¹.

Results and discussion

Characteristics of the precursor thin film

A precursor film prepared by spin-coating on a soda-lime glass (SLG) substrate and air drying at 300 °C showed a uniform, dense, and pinhole-free morphology (Fig. 1(a)). Because no crystalline peak appeared in the XRD pattern of the film (Fig. 1(b)), the film was concluded to be amorphous. The AES depth profile of a precursor film deposited on a Mo/SLG substrate reveals a uniform distribution of iron and oxygen atoms across the entire film depth (Fig. 1(c)). In addition to obtaining information regarding the iron and oxygen content, it was essential to investigate the presence of any carbon in the precursor film because the choice of the iron acetate/ethanolamine combination is largely based on its potential for fabricating carbon-free films. The absence of a carbon signal in the AES data of the film (Fig. 1(c)) confirms the facile thermal decomposition characteristics of the iron acetate/ethanolamine ink, ensuring the carbon-free nature of the synthesized precursor film.

Estimation of partial pressure of sulfur during sulfurization

As described in the Experimental section, the main experimental variables in this work are the sulfurization temperature and pressure typically set at room temperature. However, it should be noticed that the actual partial pressure of sulfur, which has more practical meaning for conversion of oxide precursors to sulfide films than the background pressure of nitrogen, under each experimental condition should be
During the sulfurization, the total gas pressure in the chamber will increase due to the increase in the nitrogen gas pressure as well as the generation of sulfur vapor. The partial pressure of sulfur inside the container will be very high if the container is completely sealed \( (P_{S,b}) \), reaching 1200 Torr even at 250 °C. However, because the lid of the container is not completely sealed, it allows the part of the high pressure gas molecules inside the container to move out. This equilibration process continues until the pressure inside the container becomes equal to that outside. One more point to be considered is the pressure limit set by the pressure relief valve by which the total pressure during sulfurization is not allowed to exceed 760 Torr. Once the total pressure is higher than this limit, part of the gas molecules in the chamber will be exhausted through the valve to maintain the total pressure to be 760 Torr. It is important to consider that all of these factors influence the actual partial pressure of sulfur in the container and should be considered for estimation.

The actual partial pressures of sulfur \( (P_{S,eq,actual}) \) estimated considering all the factors described above under selected conditions of different temperatures and background pressures are summarized in Table 1. The total pressure in the chamber \( (P_{total}) \) and partial pressure of sulfur \( (P_{S,eq}) \) calculated without considering the pressure limit are also shown. (Detailed calculation procedures are provided in the ESI, S1.†)

For temperature effects, due to the pressure limit, it is noticeable that \( P_{S,eq,actual} \) values at all temperatures are the same as 378.5 Torr. Thus, it can be considered that the phase evolution behavior in this case is indeed temperature dependent under the same partial pressure of sulfur. For the case of \( P_{N,RT} \) effects, \( P_{total} \) under a \( P_{N,RT} \) of \( 10^{-3} \) Torr is lower than the pressure limit. Therefore, \( P_{S,eq} \) is equal to \( P_{S,eq,actual} = 206.9 \) Torr, and it is expected that we can investigate the effects of different sulfur partial pressures of approximately 207 and 380 Torr at 450 °C on the phase evolution.

### Phase evolution behavior of pyrite thin films

Fig. 2 shows the morphologies of films sulfurized at different temperatures. The Raman spectra of the films are also estimated for clear understanding of the effect of experimental variables on the phase evolution behavior.

To this end, we performed quantitative analysis on the actual partial pressure of sulfur at a given temperature and background pressure of nitrogen gas, mostly referred from ref. 29. The temperature and pressure conditions chosen here are those applied to the experimental investigation which will be described in the next section. The background pressure of nitrogen at room temperature, \( P_{N,RT} \), is defined as the pressure regulated by nitrogen gas injection prior to heating, and this is typically used as an experimental variable for pressure. Upon heating, sulfur vapor is generated by evaporation and we assumed that all the solid sulfur in the container was evaporated at temperatures higher than 250 °C, supported by the absence of the remaining solid sulfur after the experiments.

### Table 1  
Estimation of \( P_{S,eq,actual} \) under selected conditions

<table>
<thead>
<tr>
<th>Background pressure ( (P_{N,RT}) ) effects ( (Temp. = 450 °C) )</th>
<th>Temperature effects ( (P_{N,RT} = 760 \text{ Torr}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 10^{-3} )</td>
<td>760</td>
</tr>
<tr>
<td>( P_{total} )</td>
<td>1449.0</td>
</tr>
<tr>
<td>( P_{S,eq} )</td>
<td>722.5</td>
</tr>
<tr>
<td>( P_{S,eq}/P_{total} )</td>
<td>0.498</td>
</tr>
<tr>
<td>( P_{total,actual} )</td>
<td>760</td>
</tr>
<tr>
<td>( P_{S,eq,actual} )</td>
<td>378.5</td>
</tr>
</tbody>
</table>

\( a \) Unit of pressure: Torr.
presented in Fig. 3. In all cases, the initial background pressure at room temperature ($P_{N,RT}$) was adjusted to 760 Torr by the injection of nitrogen gas. At 250 °C, a small-grained film consisting of marcasite (Raman peak at 323 cm$^{-1}$) and pyrite (at 347, 379 and 430 cm$^{-1}$) phases was observed, with elemental sulfur (8 at 153, 219, 246, and 472 cm$^{-1}$) partially redeposited on the surface owing to the insufficiently high temperature (Fig. 2(a) and 3). Increasing the temperature enhanced the diffusion of sulfur into the precursor films, which led to significant grain growth, as shown in Fig. 2(b) and (c). It is noted that the Raman intensity of pyrite increased with temperature, whereas that of marcasite showed the opposite trend. This finding strongly supports the notion that marcasite, the low-temperature polymorph of pyrite, first forms at low temperature and then transforms into pyrite as the temperature increases. As indicated by the Raman spectra, a temperature of 450 °C is sufficient to complete the conversion to phase-pure pyrite. The formation of pyrite via the intermediate marcasite phase is further evidenced by the compositional data of the sample, shown in Fig. 4(b), which demonstrate an abrupt drop in the S/Fe ratio to approximately 1 at 500 °C from 2 at 450 °C. The results suggest that pyrite decomposed at 500 °C even under the near-atmospheric-pressure conditions.

As the sulfurization step proceeded at 450 °C Raman peaks corresponding to marcasite disappeared, whereas the pyrite peaks gradually increased in intensity, which is consistent well with the aforementioned explanation (Fig. S2 in the ES$^i$†). A further increase in temperature to 500 °C resulted in further enhanced grain growth and film densification (Fig. 2(d)), but no Raman peak could be detected from this film (Fig. 3). On the other hand, the XRD pattern of the same sample (Fig. 4(a)) clearly revealed peaks corresponding to pyrrhotite, which is a metallic phase with the chemical formula Fe$_{1-x}$S (typically, $x = 0$ to 0.2). This discrepancy can be attributed to the structural symmetry of this phase.$^{30,31}$ The formation of pyrrhotite was further evidenced by the compositional data of the sample, shown in Fig. 4(b), which demonstrate an abrupt drop in the S/Fe ratio to approximately 1 at 500 °C from 2 at 450 °C. The results suggest that pyrite decomposed at 500 °C even under the near-atmospheric-pressure conditions.

The thermal decomposition of pyrite at high temperature motivated us to investigate the effects of pressure on the phase stability of pyrite. To this end, while maintaining the same sulfurization temperature of 450 °C, at which it was possible to obtain single-phase pyrite under 760 Torr, the effects of pressure on the crystalline structure of the sulfurized films were investigated. Here, the experimental variable for pressure is the initial background pressure at room temperature ($P_{N,RT}$). However, it is more insightful to consider the actual partial pressure of sulfur, $P_{S,eq,actual}$ calculated in the previous section. Fig. 5 clearly demonstrates that pyrite decomposed to pyrrhotite, even at 450 °C, when $P_{N,RT}$ was reduced to 10$^{-3}$ Torr ($P_{S,eq,actual} = 207$ Torr). Therefore, it should be stressed that, due to the thermal instability of the pyrite phase, the process

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**Fig. 2** Planar and cross-sectional SEM images of samples sulfurized at (a) 250 °C, (b) 350 °C, (c) 450 °C, and (d) 500 °C. The initial chamber pressure was adjusted to 760 Torr in all cases.

**Fig. 3** Raman spectra of samples sulfurized at different temperatures. The initial chamber pressure was adjusted to 760 Torr in all cases.

**Fig. 4** (a) XRD patterns and (b) S/Fe ratios of the samples sulfurized at 450 and 500 °C. The initial chamber pressure was adjusted to 760 Torr in all cases.
variables such as sulfurization temperature and pressure should be carefully chosen to suppress the decomposition of pyrite.

The composition of the single-phase FeS$_2$ film synthesized by sulfurization at 450 °C under 760 Torr was further investigated by AES analysis. Fig. 6 shows that the film contained a uniform distribution of Fe and S, with an Fe/S ratio of approximately 2. In addition, it is clear that the C and O signals were small, indicating that the iron oxide precursor film was completely converted to an iron sulfide phase with a negligible content of carbon impurities due to sulfurization.

**Optical and electrical properties of the single phase FeS$_2$ film**

The optical band gap of the synthesized single-phase pyrite film was determined by transmittance measurements. The fittings shown in Fig. 7 reveal an indirect band gap of 0.94 eV with subgap optical absorption and a direct band gap of 1.24 eV. These values are in good agreement with the most commonly accepted band-gap values for pyrite.$^{1,5,7,31}$

To further explore the applicability of the pyrite film as an absorbing material for photovoltaics, a photoelectrochemical measurement was performed on the pyrite film formed on a Mo/SLG substrate in a deaerated pH 6.5 buffer solution. This electrolyte was chosen to ensure the stability of the pyrite film during electrochemical experiments based on a potential–pH diagram for the iron–sulfur–water system (Fig. S3 in the ESI†). The stability of the pyrite film was confirmed by comparing the Raman spectra of the film taken before and after the electrochemical measurement (Fig. S4 in the ESI†). Fig. S4† shows that the two Raman spectra are identical, with no peak from any of the iron oxides or oxyhydroxides that may have possibly formed, supporting our claim that the pyrite film was highly stable in this solution. Fig. 8(a) shows a transient photocurrent curve under the AM1.5 G condition measured at 0 V/SCE (corresponding to −0.24 V/SHE), which is within the stable potential range of pyrite in pH 6.5 aqueous solution. The generation of an anodic photocurrent, which is transport-limited presumably due to the non-optimized hole-scavenging characteristics of the electrolyte used in this study, was clearly observed upon illumination. When the light was turned off, the current density returned to its original value measured in the dark. The photocurrent response could be reproduced over repeated light on/off cycles, indicating the synthesized pyrite film’s great potential for application as a solar-cell absorbing material.

The fact that we obtained an anodic photocurrent, as shown in Fig. 8(a), motivated us to further investigate the semiconducting properties of our pyrite film because a strong “anodic” photocurrent implies the possibility that the film is n-type. It is notable that most papers on the synthesis of pyrite films have ubiquitously reported p-type conductivity with low mobility,$^{7,32–34}$ whereas undoped pyrite single crystals are n-type.$^{35,36}$ In general, the low mobility of synthesized pyrite thin films has prevented the semiconducting behavior thereof from being easily determined by typical Hall measurements, and only by other techniques such as thermopower measurements has it been possible to determine the dominant charge carrier type.$^{5,7}$ Our pyrite films also showed excessively low mobility for determining the charge carrier type from Hall measurements. Therefore, we performed an electrochemical Mott–Schottky measurement on our pyrite film formed on a Mo/SLG substrate. This measurement was performed in the same deaerated pH 6.5 buffer solution used previously. The representative C$^{-2}$ vs. V curve measured from 0.1 to −0.4 V/SCE is presented in Fig. 8(b). This potential range corresponds to the stability region of the pyrite phase in a deaerated aqueous pH 6.5 solution. Fig. 8(b) depicts a straight line with a positive slope within the measured potential range, clearly reflecting the n-type behavior of the film. To the best of the authors’ knowledge, this is the first report of the n-type conductivity for a synthesized pyrite thin film.
measured by electrochemical methods. The reason for this discrepancy, compared to the ubiquitously reported p-type conductivity of most pyrite thin films, is not yet clear. First, it should be clearly understood whether this discrepancy is derived from the different measurement methods used to determine the dominant charge carrier type (electrochemical capacitance measurement in aqueous solution vs. thermopower measurements) or the film itself, which can be synthesized through a variety of different routes/sources. For the latter case, the existence of type-inversion layers on synthesized pyrite films has been proposed to explain the (reported) universal p-type characteristics of pyrite films in spite of the distinct n-type behavior of single-crystal pyrite.

A solid state device was also fabricated using the film synthesized in this study. Regarding this subject, there have been, to the best of the authors' knowledge, only two papers reporting solid state devices demonstrating reasonable rectifying I–V characteristics even with the lack of photoresponse and/or photovoltage. Fig. 9 shows dark I–V curves of the two devices built with our single phase pyrite film; one is an ITO/ZnO/Cds/FeS2/MoO3/Al device and the other is an Al/FeS2/Al device. While the Al/FeS2/Al device shows an ohmic behavior the ITO/ZnO/Cds/FeS2/MoO3/Al device demonstrates a clear rectifying character. Unfortunately, we could not detect any photovoltage from the ITO/ZnO/Cds/FeS2/MoO3/Al device under illumination. We attribute this absence of photovoltage to the imperfection of carrier transport at interfaces surrounding the pyrite film, the Cds/FeS2/MoO3 interfaces, because there was a clear photoresponse of our pyrite film in photoelectrochemical measurement (Fig. 8(a)). Clearly, more sophisticated studies on this matter should be performed including not only deeper understanding on the characteristics of the pyrite film itself but also attempts for finding optimum junction partner materials with controlled carrier transport characteristics at each interface.

Conclusions

In summary, we report an approach for fabricating pyrite (cubic FeS2) thin films via a non-vacuum, direct solution coating route using iron acetate dissolved in ethanol as a precursor solution. Amorphous iron oxide precursor films deposited using the precursor ink were completely converted to phase-pure and carbon-free iron pyrite after being sulfurized at 450 °C. In particular, the phase evolution of the films during sulfurization was systematically investigated, focusing on the effects of temperature and pressure. As the temperature increased, iron oxide began to transform into marcasite (orthorhombic FeS2) and then completely converted to pyrite. Further increasing the temperature beyond 500 °C induced the decomposition of pyrite into pyrrhotite (Fe1-xS) and sulfur vapors. The decomposition was also strongly dependent on the partial pressure of sulfur: as the pressure decreased, the decomposition occurred at lower temperature. The synthesized single-phase pyrite films showed an indirect band gap of 0.93 eV, a strong anodic photocurrent based on photo-electrochemical measurements, and n-type semiconducting properties based on a Mott–Schottky analysis.

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