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Abstract approved:

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Digital printing techniques offer several advantages in manufacturing electronics such as direct writing of materials, reduction of chemical waste, and scalability. In particular, printing can significantly simplify manufacturing processes by directly defining the channel area, the gate, and the source and drain contacts, allowing for lower costs and higher throughput manufacture of Thin Film Transistors (TFTs). Pyrite (FeS₂) and ternary compound iron germanium sulfide (Fe₂GeS₄) are compound semiconductors which consist of earth abundant elements. Both materials are being studied as promising candidates for thin film photovoltaics. In this study, iron sulfide and iron germanium sulfide thin films were fabricated by ink-jet printing for the first time. The films were formed by simply inkjet printing iron and germanium salts followed by air annealing and

sulfurization. Thin films were characterized by Ultraviolet–visible spectroscopy, X-ray diffraction, Scanning electron microscopy, Atomic force microscopy and Hall-effect measurements. The characterization results indicate P-type iron sulfide and iron germanium sulfide thin films were successfully fabricated. TFTs were fabricated and characterized using inkjet printed FeS₂ thin films on SiO₂/Mo/Glass substrates. The devices clearly show linear increment of the drain current as a function drain voltage and could be modulated by varying the gate voltage. However, the TFTs seem to show ambipolar behaviors. Better understandings of defects and electrical properties are needed to develop strategies that could improve pyrite-based TFT performance.

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Iron Chalcogenide-based Thin Films Fabricated by Inkjet Printing

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Zhen Fang, Author

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CHAPTER 1 Introduction

1.1 Inorganic p-type transistor

A semiconductor is a kind of materials that has an electrical conductivity between conductor and insulator. Currently, semiconductors are the fundamental materials of electronics all over the world. Semiconducting materials have two types that the main charge carriers are electrons (n-type) and holes (p-type). For inorganic semiconducting materials, enormous success of n-type semiconductors has been achieved, especially the oxides transparent thin film transistors (TFTs). Between 2001 and 2010, there were more than 541 papers published that related to n-type oxide based TFTs.¹ The development of n-type semiconducting materials motivated the interest in p-type semiconductors.

For inorganic p-type semiconductors, most of researches are focused on solar cells. Researchers tried to apply p-type semiconductors to TFTs, however, until now there is no report about inorganic p-type TFTs with performance that can be compared with n-type TFTs except polycrystalline Silicon. Most of p-type TFTs in the literature are organic²⁻⁵ and the mobility is still low ($<2 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$).⁶ Metal oxides n-type TFTs has achieved great improvement but metal oxides p-type TFTs are mainly limited by the low hole mobilites.⁷

More recently, metal chalcogenide TFTs have been fabricated that exhibit electron mobilites in the range of $10 - 20 \text{cm}^2/(\text{V}\cdot\text{s})$.^{8,9} Metal chalcogenide is consisting of at least one chalcogen anion and at least one more metal element. The term of chalcogenide is commonly as sulphides, selenides and tellurides.¹⁰

1.2 Inkjet printing technology

Inkjet printing is a technology familiar as computer printing that creates images by propelling droplets of ink onto paper, plastic, or other substrates.¹¹ Inkjet printing's concept originated in the 19th century that Lord William Kelvin Printing's patent described about the direction of droplets through electrostatic forces.¹² In the period 1960 – 1980, the inkjet printing technology had been developed due to the computer graphics output which helped reduction in costs and size of the printers. After that, inkjet printing had become a personal printing tool. In recent years, inkjet printing has been applied as a fabrication tool in other areas, such as displays¹³, plastic electronics¹⁴, ceramic component manufacture¹⁵, and tissue engineering¹⁶. Therefore, it has become a widely used fabrication tool in materials science.^{17,18}

Inkjet printing technique offers several advantages in manufacturing electronics such as a direct writing of materials, reduction of chemical waste, and reproducibility with high-resolution scale, which are not affordable from other solution-based approaches. Especially for the TFTs fabrication, printing can significantly simplify manufacturing processes by directly defining the channel area, the gate, and the source and drain contacts, allowing for much low costs and high throughput manufacture of TFTs.

In our study, we use the Dimatix Materials Printer (DMP) from FUJIFILM shown in Figure 1.1. The DMP is suitable for using different fluids such as protein solutions or conductive polymers as ink materials. The main principle of DMP is using a voltage cycle to actuate the nozzles of cartridge that has three segments as Figure 1.2:

- 1) A negative voltage to fill the cartridge,
- 2) A positive voltage to dispense the solution in the cartridge,
- 3) The recovery of the nozzles to their original shape.

This cycle is defined by the waveform in the DMP software that can be optimized for different solutions.

We are trying to apply metal chalcogenide materials to produce p-type TFTs and we choose solution process since the low-cost and large area fabrication. In the future, the maskless and non-vacuum processes will be most efficient way to reduce the manufacturing cost. This will lead printing technology a more potential process than conventional solution process. In this point, we explored the applying inkjet printing to metal chalcogenide p-type TFTs.

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Figure 1.1: The Dimatix Materials Printer from FUJIFILM



Figure 1.2: Actuation of the piezo-driven nozzle.

CHAPTER 2

Iron pyrite p-type semiconductor

2.1 Introduction

Iron pyrite (FeS₂) got its first attention because of its metallic luster that mimics gold, then has been researched for its optical and electrical properties. The majority of the reports about pyrite is about producing thin film for solar absorbers. Pyrite has an appropriate indirect optical band gap about 0.9eV and a high strong absorption coefficient exceeding 10^5 cm⁻¹ for hv > 1.3-1.4 eV.¹⁻³ The low band gap introduce the low open-circuit voltage of pyrite devices that affects the devices performance.¹

Pyrite thin films have been fabricated by both solution-phase and gas-phase methods for solar cell applications. Solution methods are ideal for pyrite deposition because of atmospheric pressure, low deposition temperature and large area processing including electrodeposition,⁴⁻⁶ spray pyrolysis,^{7,8} chemical bath deposition,^{9,10} and sol gel chemistry.¹¹⁻¹³ Most of these methods follow the process that is to deposit a film of iron oxides or iron sulfides then post-deposition sulfurization.

Iron pyrite hasn't been applied to thin film transistors since it has attracted mostly attention for photovoltaic applications for its very high absorption coefficient. Iron pyrite has suitable electrical properties and the composition of abundant, cheap, and non-toxic elements that can also be a potential candidate for p-type TFTs. In this study, we fabricated FeS₂ thin films by ink-jet printing of iron salt-based inks followed by air annealing and sulfurization. Thin films are characterized by UV-VIS, XRD and Hall-effect measurements. TFTs were fabricated and characterized using inkjet printed FeS₂ thin films on patterned substrates.

2.2 Experimental Methods

2.2.1 Precursor synthesis

For the ink preparation, solid $Fe(NO_3)_3$ ·9 H₂O (Sigma-Aldrich, ACS, 98+%) was dissolved into 2-methoxyethanol(Fisher Scientific, ACS, anhydrous) solvent, and the solution was then stirred at room temperature for 24hrs. The transparent red precursor was successfully formed without adding any additives.

2.2.2 Thin film preparation and analysis

Precursor was filled in plastic cartridge for FUJIFILM Dimatix Materials Printer (Fujifilm, Dimatix DMP-2831). Stable ink droplets were ejected through nozzles mounted on a printer cartridge by setting 11.5 µs and 24 V pulse at a frequency of 20 kHz. The printed film was annealed at 300 °C in air for 1 hr. to form iron oxides film. All substrates were cleaned by acetone, methanol, and DI water, then oxygen plasma (Plasma Etch Inc, PE-50) treatment for increasing wet ability. The film was printed on soda lime glass substrates for analysing band gap, and electrical properties, while SiO₂/Si substrate was used for XRD, AFM analysis and SEM. For device fabrication, film was printed on pre-patterned SiO₂/Mo/Glass test keys.

The iron oxides film was sulfurized in tube furnace (MTI, OTF-1200X) in N₂. To explore the effects of sulfurization process of the thin films, the iron oxides films were sulfurized at temperatures between 350° C and 550° C for 1hr.

Optical band gaps were determined by absorption data collected by UV-Vis using a light source of DH-2000 from Mikropack. The Hall effect measurements (Ecopia, HMS-5000) were used to evaluate the electrical properties of the iron sulfides thin films.

Film morphology was characterized by scanning electron microscopy and atomic force microscopy.

2.2.3 Thin film transistor devices fabrication and characterization

The precursor was printed on the SiO₂/Mo/Glass substrates from AUO Company as Figure 2.1, and annealed in air at 300°C for 1hr then sulfurized in N₂ at different temperatures for 1hr. The structure of the TFTs we used was bottom gate with top Source/Drain as Figure 2.2. The Source/Drain were deposited by metal thermal evaporation system from Veeco, and gold was used as material of S/D. The probing station RF-1 from CASCADE was applied to measure the performance of the TFTs. The voltage applied to gate is from 10 ~ -40V and the voltage applied to drain is from 0 ~ -40V.

2.3 **Results and Discussion**

2.3.1 Pyrite thin film characterization

 FeS_2 films were prepared on soda lime glass substrates and characterized by UV-VIS, XRD, SEM and AFM. The UV-VIS was performed to measure the band gap of the thin film shown in Figure 2.3. The film was produced by 0.1M iron nitrate precursor and sulfurized at 550°C. The band gap of the film was measured to be around 0.9eV that is identical as the reference mentioned in the introduction part.

To identify the film, XRD was applied to measure the crystallinity of the film. The printed precursor and iron oxides were measured by XRD, and both of them didn't show any peak in Figure 2.4. According to P. Melnikov's report, under high temperature that higher than 300°C annealing of iron nitrate, it should form Fe₂O₃.¹⁴ The process is:

 $Fe(NO_3)_3 \cdot 9H_2O = Fe(NO_3)_3 (s) + 9 H_2O (g),$

$$4 \operatorname{Fe}(\operatorname{NO}_3)_3(s) = 2 \operatorname{Fe}_2 O_3(s) + 12 \operatorname{NO}_2(g) + 3 O_2(g)$$

The iron oxides annealed at 300°C should be amorphous in our result. Then the oxides film was sulfurized in tubing furnace. The process is:

 $2 \operatorname{Fe}_2 O_3(s) + 11 \operatorname{S}(s) = 4 \operatorname{Fe} S_2(s) + 3 \operatorname{SO}_2(g), \quad \Delta G = -3004 + 1.06 \operatorname{T} kJ/mol.$

The XRD patterns of sulfurized thin films produced by 0.1M precursor with different sulfurization temperatures are shown in Figure 2.5. The main peak at θ =33 is the evidence for the iron pyrite films. The sulfurization temperature affects the crystallinity of the pyrite thin film. A. Yamamoto mentioned that when the sulfurization temperature is higher than 700°C the pyrite would decompose and when it is lower than 400°C there would be the formation of marcasite, the other phase of iron pyrite.¹⁵ The crystal structure of pyrite and marcasite are shown in Figure 2.6.¹⁶ Shown in the Figure 2.4, the thin film sulfurized at 550°C formed single phase of iron pyrite phase without detectable marcasite phase. As the sulfurization temperature decreased from 450°C to 350°C, the marcasite phase hasn't been detected. The intensity of the main pyrite peak at

 θ =33 decreased when the sulfurization temperature decreased. This result suggests that higher sulfurization temperature can improve the crystallinity of pyrite thin film.

2.3.2 Pyrite thin film morphology analysis

FeS₂ thin film was deposited on SiO₂/Si substrate to study its morphology by using SEM and AFM. In the Figure 2.7 and 2.8, the printed precursor film and iron oxides films are uniform and smooth. There appears the evidence of the films we printed have high quality. From Figure 2.9 to Figure 2.13, the sulfurization temperature was increased from 350°C to 550°C. At low temperature, the film shows the start of nucleation with poor crystallinity. When the annealing temperature increased, more and more particles can be seen in the images. Grains can be observed clearly after sulfurization at 400°C and the distribution of the grains became more uniform. At this sulfurization temperature, the film is mixed by both large grains and small grains. At temperatures that are higher than 500°C, it's hard to see the isolated grains, and the surface become more smooth with the roughness measured by AFM decreased from 43.8nm to 3.36nm. The grains are larger and more uniform in sizes for films annealed at 500°C. It can be confirmed that the density of grain boundaries decreased with increasing sulfurization temperature and the film of pyrite obtained by high temperature sulfurized is polycrystalline.

We decreased the precursor concentration from 0.05M to 0.01M to research how it affects the surface morphology. The sulfurization temperature used in this series of experiments was 350°C. From Figure 2.14 to Figure 2.18 the roughness of the thin films decreased from 20.4nm to 3.65nm since the grain size was getting smaller. The number of isolated grains decreased and the films became more smooth.

2.3.3 Pyrite thin film electrical properties

FeS₂ thin film was deposited on soda lime glasses to determine Hall effect mobility. The carrier concentration, electrical resistivity, Hall mobility and average Hall coefficient of the pyrite thin films sulfurized at different temperatures are shown in Table 2.1. The Hall effect measurement showed p-type conductivity by positive Hall coefficient and highest Hall mobility obtained was $4.22 \text{cm}^2 \text{V}^{-1} \text{S}^{-1}$ at 350°C in Figure 2.15. From 350°C to 450°C, the mobility decreased and the carrier concentration decreased with sulfurization temperature increasing. It could be caused by more sulfur atoms was forced into the crystal lattice of pyrite avoiding sulfur vacancy that could induce n-carrier. At 500°C, the carrier concentration dramatically increased that could be due to large grains and better crystallinity that could help to decrease the density of point defects.

2.3.4 Performance of pyrite thin film TFTs

Pyrite has been researched as solar cells for decades, however there hasn't been any report about applying pyrite as a channel layer for thin film transistors. In our study, pyrite was used to fabricate p-channel TFTs. The substrates we used were prepatterned SiO₂/Mo/glass fabricated by AUO company. The pyrite thin films were produced by 0.1 M precursor and sulfurized at different temperatures from 350°C to 550°C. The I_D/V_D curves measured by TFT probing station show in Figure 2.20. The devices indicated the channel is too conductive and poorly controlled under varied gate voltages. For high temperature, the high conductivity could be caused by the large grains and the decrease of the grains boundaries. For low temperature, the film is too conductive because the film is ambipolar that has too many electron carriers.

To optimize the devices performance, we investigated the varied concentration precursors that would change the thickness of the thin films and grain size of pyrite. In Figure 2.21, the I_D/V_D curves shows the device performance of different concentration precursors from 0.05M to 0.01M. Since the thin film sulfurized at 350°C in Section 2.3.3 had highest Hall mobility, 350°C was applied to these devices. The devices still showed highly conductive and poor gate modulation. The device produced by 0.01M precursor showed better gate control and lowest leakage current at $V_G = 0V$. The 0.01M device possessed a very thin film channel layer that helped to decrease the carrier concentration, probably due to the interfaces. In the SEM image of this sample, the FeS_2 film seems to be more smooth and had smaller grain size. The field effect mobility of this device is 1.15 cm²V⁻¹S⁻¹ and on/off ratio is about 7.0×10^2 . However, the drain current could not reach saturation that might be due to the sulfur insufficiency leading to higher electron concentration. In Figure 2.22, n-type and p-type characteristics were shown in TFTs fabricated using a precursor at 0.02M concentration. It was found that this device showed ambiploar properties in which both electrons and holes serve as charge carriers. The device exhibited high conductivity with non-saturated drain current for both n-type and ptype character that caused by the sulfur insufficiency. The non-saturated current curves are commonly observed in other reported ambipolar TFTs.^{17,18} To obtain the saturated TFTs, one potential approach is to introduce Ge or Si to form a ternary iron chalcogenide that has better stable crystal structure and stoichiometric form and we could also use Schottky barrier S/D to block the electron.

2.4 Summary

The iron pyrite (FeS₂) thin film has been successfully produced by inkjet printing and characterized by UV-VIS and XRD. The thin films morphology was analyzed by SEM and AFM for films fabricated at different sulfurization temperatures and different concentration precursors. At high sulfurization temperature, the films showed more dense and smooth morphology with larger grains. At low sulfurization temperature, the films showed isolated grains and rough. The lower concentration precursor can help to improve the films sulfurized at lower temperatures. The iron pyrite thin films were used to fabricate TFTs. However, the channels appeared to be highly conductive with poor gate control. By decreasing the precursor concentration the device performance could be improved but the drain current could not reach saturation. This may be due to the sulfur deficiency leading to high electron concentration and both n- and p- carriers. To improve the device performance, the introduction of dopants such as Sn could be applied to improve the electrical properties.

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Figure 2.1: The printed pattern for device fabrication on SiO₂ substrate.



Figure 2.2: The structure of bottom gate and top S/D TFTs.



Figure 2.3: Bang gap of FeS_2 thin film. This thin film was produced by 0.1M precursor and sulfurized at 550°C.



Figure 2.4: The printed precursor and iron oxides films were measured by XRD.



Figure 2.5: XRD shows the crystallinity of iron pyrite (JCPDS 71-0053). The film was produced by 0.1M precursor sulfurized from 550°C to 350°C.



Figure 2.6: The crystal structure of pyrite and marcasite. The pyrite is cubic and

marcasite is orthorhombic.¹⁶



Figure 2.7: The morphology of the printed precursor film produced by 0.1M precursor dried at 120°C. (a) SEM image of the thin film. (b) AFM image of the thin film, the roughness is 0.585nm.



Figure 2.8: The morphology of the iron oxides film produced by 0.1M precursor annealed at 300°C. (a) SEM image of the thin film. (b) AFM image of the thin film, the roughness is 0.439nm.



Figure 2.9: The morphology of the pyrite thin film produced by 0.1M precursor sulfurized at 350°C. (a) SEM image of the thin film. (b) AFM image of the thin film, the roughness is 43.8nm.



Figure 2.10: The morphology of the pyrite thin film produced by 0.1M precursor sulfurized at 400°C. (a) SEM image of the thin film. (b) AFM image of the thin film, the roughness is 6.49nm.



Figure 2.11: The morphology of the pyrite thin film produced by 0.1M precursor sulfurized at 450°C. (a) SEM image of the thin film. (b) AFM image of the thin film, the roughness is 2.35nm.



Figure 2.12: The morphology of the pyrite thin film produced by 0.1M precursor sulfurized at 500°C. (a) SEM image of the thin film. (b) AFM image of the thin film, the roughness is 3.14nm.



Figure 2.13: The morphology of the pyrite thin film produced by 0.1M precursor sulfurized at 550°C. (a) SEM image of the thin film. (b) AFM image of the thin film, the roughness is 3.36nm.



Figure 2.14: The morphology of the pyrite thin film produced by 0.05M precursor sulfurized at 350°C. (a) SEM image of the thin film. (b) AFM image of the thin film, the roughness is 20.4nm.



Figure 2.15: The morphology of the pyrite thin film produced by 0.04M precursor sulfurized at 350°C. (a) SEM image of the thin film. (b) AFM image of the thin film, the roughness is 24.8nm.



Figure 2.16: The morphology of the pyrite thin film produced by 0.03M precursor sulfurized at 350°C. (a) SEM image of the thin film. (b) AFM image of the thin film, the roughness is 10.9nm.



Figure 2.17: The morphology of the pyrite thin film produced by 0.02M precursor sulfurized at 350°C. (a) SEM image of the thin film. (b) AFM image of the thin film, the roughness is 11.5nm.



Figure 2.18: The morphology of the pyrite thin film produced by 0.01M precursor sulfurized at 350°C. (a) SEM image of the thin film. (b) AFM image of the thin film, the roughness is 3.65nm.



Figure 2.19: Hall effect measurement of different sulfurization temperatures. The film was produced by 0.1M precursor sulfurized from 350°C to 550°C.







Figure 2.20: I_D/V_D plots measured by TFT probing station. The thin films were produced by 0.1M precursor at different sulfurization temperatures: (a) 350°C, (b) 400°C, (c) 450°C, (d) 500°C, (e) 550°C.



Figure 2.21: I_D/V_D plots measured by TFT probing station. The thin films were produced by different concentration precursors at 350°C sulfurization temperature: (a) 0.05M, (b)

0.04M, (c) 0.03M, (d) 0.02M, (e) 0.01M.



Figure 2.22: I_D/V_D plots measured by TFT probing station. The thin film was produced by 0.02M precursor and sulfurized at 350°C. (a) the device was measured as n-type TFTs, (b) the device was measured as p-type TFTs.

Temperature (°C)	Carrier Concentration (/cm ³)	Resistivity (Ωcm)	Mobility (cm ² /VS)	Average Hall Coefficient (cm ³ /C)
350	7.34×10^{18}	2.01	4.22	0.850
400	1.18×10^{17}	26.7	1.96	52.3
450	3.72×10^{16}	107	1.57	77.0
500	1.87×10^{20}	0.223	0.145	0.0334
550	4.24×10^{19}	0.113	1.30	0.147

Table 2.1: The result of Hall effect measurement for pyrite thin film sulfurized at

different temperatures.

CHAPTER 3

Inkjet printed Fe₂GeS₄ p-type semiconductor

3.1 Introduction

Iron chalcogenides have great potential to be thin film transistors materials. However, iron pyrite shows too conductive as a channel layer for TFTs. Yu suggested that iron pyrite with sulfur deficient phase are more stable than stoichiometric FeS_2 .¹ To solve this problem, they introduced Fe_2XS_4 (X = Ge, Si) as alternative materials of iron pyrite that could have same properties as iron pyrite. Ternary iron chalcogenide have significantly better stability.

The optical band gap of iron pyrite is about 0.9eV. However, the defects in the sulfur sublattice create states inside the band gap leading to a small band gap.²⁻⁵ The band gaps of Fe_2XS_4 are larger than those of pyrite, that the band gap for Ge is 1.40eV and the band gap for Si is 1.55eV. With these more stable ternary and higher band gap ternary iron chalcogenide, the too conductive issue of pyrite may be solved.

In our study, we fabricated Fe_2GeS_4 thin films by ink-jet printing of iron saltbased inks with germanium iodide followed by air annealing and sulfurization. Thin films are characterized by UV-VIS, XRD, Hall-effect measurements, SEM and AFM.

3.2 Experimental Methods

3.2.1 Precursor synthesis

For the ink preparation, solid Fe(NO₃)₃·9 H₂O (Sigma-Aldrich, ACS, 98+%) and GeI₄ (Sigma-Aldrich, ACS, 99.99%) was dissolved into 2-methoxyethanol(Fisher Scientific, ACS, anhydrous) solvent, and the solution was then stirred at room

temperature for 24hrs. The dark red precursor was successfully formed without adding any additives.

3.2.2 Thin film preparation and analysis

Precursor was filled in plastic cartridge for FUJIFILM Dimatix Materials Printer (Fujifilm, Dimatix DMP-2831). Stable ink droplets were ejected through nozzles mounted on a printer cartridge by setting 11.5 µs and 24 V pulse at a frequency of 20 kHz. The printed film in Figure 3.1 was annealed at 300 °C in air for 1 hr to form iron oxides film. All substrates were cleaned by acetone, methanol, and DI water, then oxygen plasma (Plasma Etch Inc, PE-50) treatment for increasing wet ability. The film was printed on soda lime glass substrates for analysing band gap, and electrical properties, while SiO₂/Si substrate was used for XRD, AFM analysis and SEM.

The iron germanium oxides film was sulfurized in tube furnace (MTI, OTF-1200X) in N₂. To explore the effects of sulfurization process of the thin films, the iron oxides films were sulfurized at temperatures between 350°C and 550°C for 1hr. The crystallinity of sulfurized thin films was identified by XRD.

Optical band gaps were determined by absorption data collected by UV-Vis using a light source of DH-2000 from Mikropack. The Hall effect measurements (Ecopia, HMS-5000) were used to evaluate the electrical properties of the iron sulfides thin films.

Film morphology was characterized by scanning electron microscopy and atomic force microscopy.

3.3 Results and Discussion

3.3.1 Iron Germanium sulfide thin film characterization

Fe₂GeS₄ films were prepared on soda lime glass substrates and characterized by UV-VIS, XRD, SEM and AFM. The UV-VIS was performed to measure the band gap of the thin film. The film was produced by 0.1M iron nitrate and 0.05M germanium iodide precursor and sulfurized at 550°C. The band gap of the film was measured to be around 1.4eV in Figure 3.2 that is identical as the reference mentioned in the introduction part.

To identify the film, XRD was applied to measure the crystallinity of the film. The printed precursor and iron oxides were measured by XRD, and both of them didn't show any peak in Figure 3.4. The printed precursor films were annealed at 300°C. The process is:

> $Fe(NO_3)_3 \cdot 9H_2O = Fe(NO_3)_3 (s) + 9 H_2O (g),$ 4 Fe(NO_3)_3 (s) = 2 Fe₂O₃ (s) + 12 NO₂ (g) + 3 O₂ (g), GeI_4 + 2 H_2O (g) = GeO_2 (s) + 4 HI (g).

Then the oxides film was sulfurized in the tubing furnace at different temperatures. The process is:

$$2 \operatorname{Fe_2O_3}(s) + 11 \operatorname{S}(s) = 4 \operatorname{FeS_2}(s) + 3 \operatorname{SO_2}(g), \quad \Delta G = -3004 + 1.06 \operatorname{T} kJ/mol, \quad (1)$$

$$2 \operatorname{Fe_2O_3} + 7 \operatorname{S}(g) = 4 \operatorname{FeS}(s) + 3 \operatorname{SO_2}(g), \quad \Delta G = -1582.4 + 0.274 \operatorname{T} kJ/mol,$$
 (2)

$$GeO_2(s) + 3 S(g) = GeS_2(g) + SO_2(g), \qquad \Delta G = -442.3 + 0.0595T \text{ kJ/mol}, \qquad (3)$$

$$GeO_2(s) + 2S(g) = GeS(s) + SO_2(g), \qquad \Delta G = -340.2 + 0.0561T \text{ kJ/mol}, \quad (4)$$

In this process, there are 4 different mid-reactions from (1) to (4). For the sulfurization of iron oxide, even the reaction (1) has lower Gibbs free energy, but we assume for the next step reaction the activation energies of both them are similar. In this point, the mid-reaction tends to form the product that has higher Gibbs free energy, so we think the reaction (2) is what happened during the reaction. In this process, the GeS₂ vapor could be a favorable reagent for the final reaction with FeS to form Fe₂GeS₄, so the mid-reactions should be (2) + (3). The final reaction is

$$2 \text{ FeS}(s) + \text{GeS}_2(g) = \text{Fe}_2\text{GeS}_4(s).$$

The crystal structure of Fe₂GeS₄ is the olivine structure same as Fe₂SiS₄ in the Figure 3.3.⁶ In the crystal structure, half of the octahedral sites are filled by Fe²⁺ and $\frac{1}{8}$ of the tetrahedral holes are occupied by Ge^{4+,7} The sulfurization temperature affects the crystallinity of the iron germanium sulfide thin film. In the Figure 3.5 the thin film produced by 0.1M precursor sulfurized at 350°C showed a board peak around 2 θ =30. According to the ref 8, the main peaks of Fe₂GeS₄ are at 2 θ =28, 30 and 33. This should be the mix of the peaks at 2 θ =28 and 30. For this sample, since there were no narrow peaks, the film should be amorphous. As the sulfurization temperature increased, the peak at 2 θ =33 presented after sulfurization reached 450°C. With the temperature increased, the thin film. However, this peak should be iron pyrite peak that matched pyrite pattern. The reaction system we used is an open system that GeS₂ vapor could be purged away by N₂. Then the Ge content should not be sufficient so there could be some iron pyrite formed during sulfurization.

3.3.2 Iron Germanium sulfide thin film morphology analysis

Fe₂GeS₄ thin film was deposited on SiO₂/Si to test morphology by using SEM and AFM. In the Figure 3.6 and 3.7, the printed precursor film and oxides film are smooth, uniform and pin-hole free. The roughness of both films are very small, the printed precursor film is 0.506nm and oxides film is 0.410nm. This could be the evidence that the ink-jet printed films based on our chemical have good quality.

From Figure 3.8 to Figure 3.12, the sulfurization temperature was increased from 350°C to 550°C. The roughness of the film sulfurized at 350°C is 1.63nm. After Ge was introduced into FeS₂, the thin film sulfurized at low temperature was more smoothly and tends to be amorphous that is consist with XRD results. Since the narrow peak in XRD pattern should be pyrite peak, EDX was applied to analyze the content of the films. In EDX data, Ge content can be detected in all the thin films, but the amount of Ge is not sufficient. With the temperature increasing, the nucleation started and the film showed crystalline. Fe₂GeS₄ grains can be observed clearly after sulfurized at 400°C. From EDX data, the Ge was also detected in the top grains that we can claimed that Fe₂GeS₄ grains presented. At high temperature 500°C, more and more large grains formed at the top of the films, the roughness measured by AFM increased from 1.63nm to 18.2nm and the size of the grains increased. However, not all of the grains are connected to each other and it's hard to claim that the grains are uniformly distributed. The films sulfurized at high temperature may not be suitable for TFTs, since the films are rough.

To form a dense polycrystalline film that all the grains are connected to each other, higher temperature need to be applied for Fe₂GeS₄. However, the amorphous films produced at low sulfurization temperatures would be potential as a channel layer of TFTs.

3.3.3 Iron Germanium sulfide thin film electrical properties

Fe₂GeS₄ thin film was deposited on lime glasses to test Hall effect mobility. The carrier concentration, electrical resistivity, Hall mobility and average Hall coefficient of the pyrite thin films sulfurized at different temperatures are shown in Table 3.1. The Hall effect measurement showed p-type conductivity and highest Hall mobility achieved was 8.42 cm²V⁻¹S⁻¹ at 550°C in Figure 3.1. From the 350°C to 550°C the carrier concentration decreased and the resistivity increased, that is semiconductor-like. The resistivity is mainly governed by carrier concentration since both of them have same trends with temperature increasing. The Hall mobility increased with the sulfurization temperature increasing. However, the Hall mobility of the film sulfurized at 350°C is high as 2.26 cm²V⁻¹S⁻¹. As other researchers' report, the Hall mobility is dependent on the density of crystal defects, like point defects, grain boundaries, film surface and etc.⁹ The increase in roughness could enhance the carriers scattering and decrease the Hall mobility.¹⁰ The film sulfurized at 350°C is amorphous and the roughness is small. This could be the cause that the Hall mobility of this film is high. In this case, the film sulfurized at 350°C could a very promising candidate of p-type TFTs.

3.4 Summary

Since Fe₂GeS₄ is more stable than FeS₂ and has higher band gap that could be applied to TFTs, we successfully produced Fe₂GeS₄ thin film by using inkjet printer. The band gap measured by UV-VIS was 1.4eV that mentioned in the other reports. XRD was applied to identify and measure the crystallinity of the films. The films produced at low temperature might be amorphous and presented crystalline at temperature higher than 450°C. The thin films morphology was analyzed by SEM and AFM for different sulfurization temperatures. At high sulfurization temperatures, the films showed isolated crystal on the films and rough. At low sulfurization temperatures, the films showed smooth and good film quality. In this case, the Fe₂GeS₄ thin film sulfurized at low temperature is a potential candidate of channel layer for TFTs. The Fe₂GeS₄ TFTs will be fabricated in the further research.

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Figure 3.1: The printed pattern of Fe_2GeS_4 on SiO_2 substrate.



Figure 3.2: Bang gap of Fe₂GeS₄ thin film. This thin film was produced by 0.1M 2:1 precursor and sulfurized at 550°C.



Figure 3.3: Crystal structure of Fe_2XS_4 , X = Si, $Ge^{.6}$



Figure 3.4: The printed precursor and iron germanium oxides films were measured by



Figure 3.5: XRD shows the crystallinity of Fe₂GeS₄ (JCPDS 25-0396). The film was produced by 0.1M 2 to 1 precursor sulfurized from 550°C to 350°C.



Figure 3.6: The morphology of the printed precursor film produced by 0.1M precursor dried at 120°C. (a) SEM image of the thin film. (b) AFM image of the thin film, the roughness is 0.506nm.



Figure 3.7: The morphology of iron germanium oxides film produced by 0.1M precursor annealed at 300°C. (a) SEM image of the thin film. (b) AFM image of the thin film, the

roughness is 0.410nm.



Figure 3.8: The morphology of the Fe_2GeS_4 thin film produced by 0.1M precursor sulfurized at 350°C. (a) SEM image of the thin film, EDX shows Fe:Ge = 4.09:1.33. (b) AFM image of the thin film, the roughness is 1.63nm.



Figure 3.9: The morphology of the Fe_2GeS_4 thin film produced by 0.1M precursor sulfurized at 400°C. (a) SEM image of the thin film, EDX shows Fe:Ge = 2.14: 0.34. (b)

AFM image of the thin film, the roughness is 12.0nm.



Figure 3.10: The morphology of the Fe_2GeS_4 thin film produced by 0.1M precursor sulfurized at 450°C. (a) SEM image of the thin film, EDX shows Fe:Ge = 2.73:1.04. (b) AFM image of the thin film, the roughness is 17.6nm.



Figure 3.11: The morphology of the Fe_2GeS_4 thin film produced by 0.1M precursor sulfurized at 500°C. (a) SEM image of the thin film, EDX shows bottom layer Fe:Ge = 0.6:0.34 and top crystal Fe:Ge = 1.2:0.22. (b) AFM image of the thin film, the roughness is 18.2nm.



Figure 3.12: The morphology of the Fe_2GeS_4 thin film produced by 0.1M precursor sulfurized at 550°C. (a) SEM image of the thin film, EDX shows bottom layer Fe:Ge = 1.73:0.33 and top crystal Fe:Ge = 3.6:0.63. (b) AFM image of the thin film, the roughness is 9.2nm.



Figure 3.13: Hall effect measurement of different sulfurization temperatures. The film was produced by 0.1M 2 to 1 precursor sulfurized from 350°C to 550°C.

Temperature	Carrier Concentration	Resistivity	Mobility	Average Hall
(°C)	$(/cm^{3})$	(Ωcm)	$(\text{ cm}^2/\text{VS})$	Coefficient
				(cm^{3}/C)
350	2.49×10^{18}	1.11	2.26	2.50
400	3.10×10^{17}	121	0.173	20.2
450	1.96×10^{16}	490	0.65	318
500	5.50×10^{15}	770	1.48	1140
550	6.51×10^{14}	1140	8.42	9600

Table 3.1: The result of Hall effect measurement for iron germanium sulfide thin film

sulfurized at different temperatures.