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sulfur source**

Perez, William Henry, M.S.

San Jose State University, 1992

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Ann Arbor, MI 48106

**GROWTH OF POLYCRYSTALLINE ZnS BY MOCVD
USING THIOPHENE AS A SULFUR SOURCE**

A Thesis

Presented to

**The Faculty of the Department of Materials Engineering
San Jose State University**

**In Partial Fulfillment
of the Requirements for the Degree
Master of Science**

by

William H. Perez

December, 1992

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ABSTRACT

GROWTH OF POLYCRYSTALLINE ZnS BY MOCVD USING THIOPHENE AS A SULFUR SOURCE

by William H. Perez

Deposition of ZnS thin films by MOCVD (metalorganic chemical vapor deposition) was attempted using 10% DMZn in helium and liquid thiophene (C_4H_4S) through which helium was bubbled. Growths were conducted at pressures between 1-10 torr and temperatures between 250-500°C. No ZnS deposits resulted due to short residence times of thiophene in the reaction chamber.

Deposition was also carried out using hydrogen sulfide (H_2S) in place of thiophene. Good deposits were achieved with growth rates ranging from 0.1-1.1 $\mu m/min$ over the range of parameters studied. Growth rate trends were evaluated, and the growth rate was found to be directly related to the [$H_2S + He$] flow and growth temperature. However, the growth rate was found to be inversely related to the [DMZn + He] flow, which is thought to be caused by the increased [DMZn + He] flow overwhelming the local environment of the susceptor and starving the reaction surface of H_2S .

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Table of Contents

	Page
Abstract	iii
Acknowledgements	iv
Table of Contents	v
List of Tables	vii
List of Figures	viii
I. Introduction	1
Applications of ZnS	2
Deposition Techniques	5
Atomic Layer Epitaxy	5
Molecular Beam Epitaxy	7
MOCVD of Zinc Sulfide	9
Sources used in MOCVD of ZnS	14
Zinc Sources	14
Sulfur Sources	15
Safety of Precursors Used in MOCVD of ZnS	19
Summary of MOCVD Sources for ZnS	20
Kinetics of Reactions by MOCVD	21
II. Fabrication Techniques of Zinc Sulfide Devices	23
III. Apparatus	27
IV. Procedure and Results for Thiophene	33
V. Procedure and Results for H ₂ S	37
VI. Conclusion	58

VII. References	59
VIII. Appendix	62
MOCVD Operating Procedures	63

List of Tables

	Page
1. Physical Data for the Commonly Used Sources in the Growth of Zinc Sulfide	21
2. Vapor Pressure of Thiophene as a Function of Temperature	31
3. MOCVD of ZnS Run Data using Thiophene as the Sulfur Source	36
4. MOCVD of ZnS Run Data using H ₂ S as the Sulfur Source	38

List of Figures

	Page
1. Alpha Particle Scattering.	3
2. Atomic Layer Epitaxy of ZnS.	6
3. Simplified Schematic of an MBE Reactor.	8
4. Gaseous Source MOCVD Reactor.	10
5. Gaseous and Liquid Source MOCVD Reactor.	11
6. Susceptor Geometries Used in MOCVD.	13
7. Alternative Zinc Sources for ZnS growth.	15
8. Photo-Assisted MOCVD.	17
9. Alternative Sulfur Sources for ZnS Growth.	18
10. MOCVD Apparatus	28
11. Schematic of Thiophene Line.	33
12. Surface Morphology of ZnS.	43
13. Cross-section of ZnS.	44
14. Energy Dispersive X-Ray of ZnS.	45
15. Thickness vs. Sulfur Flow at T=250°C.	46
16. Thickness vs. Sulfur Flow at T=350°C.	47
17. Thickness vs. Sulfur Flow at DMZn flow=8 sccm.	48
18. Thickness vs. Sulfur Flow at DMZn flow=10 sccm.	49
19. Thickness vs. DMZn Flow at T=250°C.	50
20. Thickness vs. DMZn Flow at T=350°C.	51
21. Thickness vs. DMZn Flow at H ₂ S Flow=16 sccm.	52

22.	Thickness vs. DMZn Flow at H2S Flow=38 sccm.	53
23.	Thickness vs. Growth Temp. at DMZn Flow=8 sccm.	54
24.	Thickness vs. Growth Temp. at DMZn Flow=10 sccm.	55
25.	Thickness vs. Growth Temp. at H2S Flow=16 sccm.	56
26.	Thickness vs. Growth Temp. at H2S Flow=38 sccm.	57

I. Introduction

Over the past 20 years, increasing work has been done with the uses of II/VI compounds such as zinc sulfide (ZnS). Today they have applications in uses calling for polycrystalline thin film layers such as thin film electroluminescent devices, as a suspension in liquids in the field of biology where they have been used for marking auto radiograms, and in the production of display screens where ZnS has been used for years for cathode ray tubes (CRT's).

They also have seen use in single crystal applications where their primary function is in blue light emitting diodes (LED's).

Recent work with ZnS is reviewed, showing the range of its applications as well as the variety of deposition techniques used to grow it, including atomic layer epitaxy (ALE), molecular beam epitaxy (MBE), and metal organic chemical vapor deposition (MOCVD), the subject of this paper.

There has been a wide variety of sources used in the growth of ZnS by MOCVD. Motivation for the uses of the common ones as well as the one which is the subject of this project, thiophene (C_4H_4S), will be discussed. Among the reasons for using this sulfur source are the safety

considerations, so the commonly used sources will be reviewed from this standpoint as well.

The objective of this project is to grow ZnS thin films using the MOCVD reactor here at San Jose State University. Other students who have used this equipment are Marc Jensen, Hoa Do, Hamid Kashani, Rex Chuang, and Richard Patten.

It is also of interest to get an idea of trends of thin film growth with the H_2S sulfur source.

Applications of Zinc Sulfide

A very important result in science, the theory of atomic structure, was postulated by Sir Ernest Rutherford with the help of zinc sulfide. Geiger and Marsden conducted backscattering experiments under the supervision of Rutherford in 1911. In their setup, a radioactive source emits α -particles which pass through a pinhole in a lead screen. The beam then passes through a thin metal foil made of gold, silver, or copper. The scattered beam from the metal foil finally hits a plate coated with zinc sulfide, where a momentary flash or scintillation is observable at each collision.^(1,2) This occurs when electrons in the material are excited from the valence band into the conduction band. When the electron drops back to the valence band, a photon is emitted. If the wavelength of this photon is in the visible range, it is called

luminescence. When there is a delay in this decay, caused by impurities resulting in energy traps between the conduction and valence bands, the luminescence is called phosphorescence.

A diagram of the experimental setup is shown in Figure 1.

Figure 1. Alpha particle scattering. Alpha particles scattered by a thin metal foil are detected when they strike a metal plate coated with zinc sulfide.⁽²⁾

When Rutherford's team examined the results of their experiments they determined that the number of α -particles scattered through large angles could not be explained by a uniform distribution of charge in the atom as theorized by J.J. Thomson. Instead, they concluded that most of the mass and charge of an atom must be concentrated in the

center of the atom, which Rutherford named the nucleus. Hence, the use of zinc sulfide helped physicists discover one of the important physical results in the 20th century.

Zinc sulfide has applications in the field of biology where it has been used for marking autoradiograms. Donald Seto, et al.⁽³⁾ at California Institute of Technology used suspensions of ZnS in water or glycerol to detect light emission. When the suspension is exposed to an incandescent light source, it will emit visible light in the green-yellow range. It is this property that makes ZnS suitable for applications such as molecular cloning techniques, radioactive nucleotide sequencing and nonradiative detecting systems such as chemiluminescent probes which may require orientation and identification markings.

The phosphorescent properties of ZnS also make it an excellent choice for display applications. Activated ZnS has been used for years in cathode ray tubes in televisions, oscilloscopes, and electron microscopes. In CRT's, the phosphorescent properties of zinc sulfide again come into play. Electrons are excited into the conduction band as before. Impurities are engineered into the zinc sulfide to cause traps resulting in photon emission with wavelengths corresponding to green, blue and red.

Zinc sulfide also displays electroluminescent properties. Electroluminescence is defined as the emission of visible light by a p - n junction across which a forward-biased voltage is applied. Electroluminescent devices are commonly manufactured using ZnS thin film layers. In the past, these films have been grown by atomic layer epitaxy (ALE), molecular beam epitaxy (MBE), and metal organic chemical vapor deposition (MOCVD).

Deposition Techniques

Deposition of thin film ZnS layers can be carried out by several techniques. Along with MOCVD, two other techniques coming into wider use are atomic layer epitaxy and molecular beam epitaxy.

Atomic Layer Epitaxy Also known as ALE, was primarily developed for the deposition of compound semiconductors, either III/V or II/VI compounds. The characteristic feature of ALE is the sequential alternating saturation of each layer grown of the compound of interest. For instance, in the growth of ZnS by ALE, first a layer of Zn would be allowed to saturate on the surface, growth would be suspended, then a layer of S would be allowed to saturate on top of the layer of Zn, growth would be suspended, then the cycle would repeat until the desired thickness is reached. In most cases, each growth step

constitutes less than a full monolayer, bringing up the importance of surface reconstruction during each step of the deposition.⁽⁵⁾ A representation of ALE is shown in Figure 2.

Figure 2. Atomic Layer Epitaxy of ZnS. Sequences of ALE process for ZnS using (a) elemental reactants (exposure to zinc vapor, chemisorption of zinc monolayer, purge of zinc surplus, exposure to S₂ vapor, chemisorption of sulfur, purge of S₂ surplus, exposure to zinc vapor etc.) and (b) compound reactants (exposure to ZnCl₂ vapor, chemisorption of ZnCl₂, purge of ZnCl₂ surplus, exposure to H₂S, exchange reaction resulting in solid ZnS and HCl, purge of HCl and surplus of H₂S, exposure to ZnCl₂ vapor, etc.).⁽⁵⁾

One of the main uses of ALE is in the deposition of ZnS layers for TFEL's. A cross section of this film is

likely to have columnar growth arising from 2-dimensional nucleation, rather than columnar growth resulting from "point nucleus" growth. In other words, defects originating from the original surface at the onset of ALE do not grow and expand as they would in point nucleus growth. Columnar growth is a common feature seen in polycrystalline layers of ZnS. It is more desirable to have columns with 2-dimensional origination since they don't expand and overlap, further reducing the crystallinity of the layers.

ALE equipment is of two types: High vacuum systems similar to an MBE chamber and CVD-type systems capable of growing at a range of pressures. The high vacuum type of systems have an advantage in being better fitted for in-situ measurements, while the CVD-type systems can more easily be scaled up to industrial applications.

Molecular Beam Epitaxy MBE has been utilized by Yoshikawa, et al.⁽⁶⁾ in their development of single-crystal ZnS and ZnSe for use as blue light emitting diodes. They used DMZn and either H₂S or H₂Se as reactants. One of the advantages of MBE is the long mean free path between collisions as a result of the high vacuum of the process. This virtually eliminates pre-reaction of the chemical species. A schematic of a typical MBE apparatus is shown in Figure 3.

Other methods, such as sputtering and vacuum deposition can be implemented much less expensively, but films of good crystallinity are much harder to produce.

Figure 3. Simplified Schematic of an MBE Reactor⁽⁷⁾.

MOCVD of Zinc Sulfide

MOCVD has become an increasingly important growth technique over the past 20 years and has expanded in use from primarily III/V work to II/VI work. It is expected that in the future MOCVD will become important in the areas of superconductors and high dielectric insulators.

Thin film growth by MOCVD has both advantages and disadvantages. It is very versatile and easily scaled up, but it can also be very expensive. Large scale production reactors, capable of handling many wafers at a time, can cost upwards of a million dollars. MOCVD reactors use both liquid and gaseous reactant sources, and much of the high cost of running an MOCVD reactor is due to the safety systems, temperature controlling systems and monitoring systems needed to safely achieve high quality thin films.

Reactant sources for MOCVD are of two varieties: A gaseous source, such as 1% dimethylzinc (DMZn) in helium; or a liquid source, such as pure liquid DMZn, through which a carrier gas is bubbled.

A schematic of an entirely gaseous source MOCVD apparatus is shown in Figure 4.

Figure 4. Gaseous Source MOCVD Reactor.
Schematic diagram of an entirely gaseous source
MOCVD reactor.⁽⁸⁾

In this diagram, the essential parts of the MOCVD apparatus are described:

Gaseous 1% DMZn in helium and 10% hydrogen sulfide (H₂S) in helium travel toward the reactor in separate gas lines. The H₂S line terminates inside the chamber so as to provide good mixing throughout, while the DMZn line terminates just above and pointing directly towards the susceptor. The susceptor temperature is automatically controlled by a thermocouple placed in the susceptor. The reactants travel across the susceptor where they increase in temperature and deposit onto the susceptor and the

substrate which is placed on the susceptor. The carrier gas along with the reacted species are exhausted out the bottom of the reactor.

The second type of MOCVD apparatus, containing one or more liquid organometallic sources is shown in Figure 5.

Figure 5. Gaseous and Liquid Source MOCVD reactor.

Schematic diagram of MOCVD reactor containing one liquid organometallic source.⁽⁹⁾

In this setup, pure helium is bubbled through a temperature-controlled DMZn bubbler, saturates with DMZn, and then travels towards the reactor inlet. The gaseous species travel toward the reactor inlet in a separate gas line and meet at the upstream edge of the reactor inlet.

The reactants flow over the susceptor, heat up and deposit onto the substrate.

In general, in MOCVD of II/VI semiconductor thin films, the group II sources, like zinc and cadmium, are kept separate from the group VI sources, like sulfur, selenium and tellurium, until they reach the reactor inlet. This is to avoid premature reactions which could cause condensation on the plumbing lines leading to the reactor.

There are also several types of susceptor geometries in use as shown in Figure 6.

Typically, horizontal- and pedestal-type geometries are capable of holding one or two wafers and are used primarily for research and development applications, while the large scale barrel- and pancake-type geometries are capable of holding up to 24 wafers.

Figure 6. Susceptor Geometries Used in MOCVD.
 Schematic representation of susceptor geometries used in MOCVD: (a) pedestal, (b) horizontal, (c) barrel, and (d) pancake.⁽¹⁰⁾

Sources Used in MOCVD of ZnS

As varied as the applications for ZnS are, and as varied as the types of deposition and doping techniques used in the growth of ZnS layers, so too are the precursor chemicals used in the production of ZnS layers.

Zn Sources. By far the most commonly used zinc compounds are DMZn and DEZn. They both are pyrophoric substances in their pure forms.

Wright and Cockayne have reported work using liquid DMZn⁽¹²⁾, as have Hirabayashi and Kogure⁽¹¹⁾, while Fujita, et al.⁽¹²⁾ have reported using both DEZn and DMZn liquids in their work. In these three cases H₂ gas was used as the carrier to transport the zinc sources to the reaction chamber. Yoshikawa⁽¹³⁾ also reports using DMZn but he chose a system using all gaseous sources of the chemical of interest mixed with helium, and helium as the ballast gas.

In cases where pre-reaction of the Zn source with H₂S is of concern, work has been reported using the chelating ligands of zinc called 1,4-dioxan and 1,4-thioxan.⁽¹⁴⁾ Use of these adducts in place of DMZn or DEZn prevented pre-reaction at low temperatures, but did not push up the susceptor temperature needed for successful growth. The structure of these compounds is shown in Figure 7.

Figure 7. Alternative Zinc Sources for ZnS Growth.
Dimethylzinc adducts of (a) 1,4-dioxan (MP 66°C) and (b) 1,4-thioxan (MP 23°C).⁽¹⁴⁾

Sulfur Sources. Sulfur sources utilized have been quite varied over the last ten years of work in this field. Hydrogen sulfide has been the chemical of choice when low growth temperature was important. Yoshikawa, et al.⁽¹³⁾ cites many reasons for his desire to use H_2S . Among them are the problems inherent in using a liquid source, such as:

- 1) possible desaturation of the bubbled species,

- 2) temperature fluctuation which affects the vapor pressure of the source,
- 3) inaccurate estimation of the amount of material left in a bubbler, and
- 4) the many valves and fittings, temperature controllers, etc. that may be needed with the use of liquid sources.

The use of liquid sulfur sources, though, has several distinct advantages over the use of H_2S .

Use of carbon disulfide was chosen by Takata, et al.,⁽¹⁵⁾ because it is less expensive than other liquid sources in use, it is easier to handle than a toxic gas like H_2S , and the problem of premature reaction is eliminated. Hirabayashi and Kozawaguchi⁽¹⁶⁾ reported using diethylsulfur. Its disadvantages are that it is expensive, and it requires a high growth temperature. They were able to take care of the high growth temperature problem by using photo-assisted deposition, which allowed them to reduce the growth temperature from $500^{\circ}C$ to $400^{\circ}C$ by irradiation, as shown in Figure 8.

Finally, the use of heterocyclic compounds has been studied in some detail by Jones, et al.⁽¹⁴⁾ They experimented with heterocyclic compounds and found that they eliminated pre-reaction of the zinc compound and the sulfur compound but the price they paid was a higher growth

temperature. The compounds they used are shown in Figure 9.

Figure 8. Photo-Assisted MOCVD. Growth temperature dependence of growth rate for ZnS:Mn film prepared with and without radiation. (16)

Figure 9. Alternative Sulfur Sources for ZnS Growth.
 Heterocyclic compounds used in the growth of ZnS, ZnSe, and ZnO: (a) thiophene (C_4H_4S); (b) tetrahydrothiophene (C_4H_8S); (c) selenophene (C_4H_4Se); (d) furan (C_4H_4O); (e) tetrahydrofuran (C_4H_8O); (f) tetrahydropyran ($C_5H_{10}O$).⁽¹⁴⁾

Safety of Precursors Used in MOCVD of ZnS.

Another factor touched upon earlier is the safety concerns of the chemicals chosen. Mixtures of DMZn in H₂ are classified as a flammable gas while mixtures of DMZn in helium are classified as a non-flammable gas. All of these mixtures should be considered to be simple asphyxiants.

DMZn and DEZn in their pure forms in liquid bubblers are classified as pyrophoric liquids. They spontaneously ignite in air and react violently in water. When pure DMZn reacts with air, zinc oxide fumes result which, when inhaled, can alter blood proteins leading to a hyperthermic reaction⁽¹⁷⁾.

Hydrogen sulfide is classified as a flammable compressed gas. It is a toxic gas with a very distinct rotten egg odor. The lowest lethal concentration published for humans is 600 ppm for 30 minutes.^(17,18) Carbon disulfide (CS₂), diethyl sulfur (DES), and thiophene (or thiofuran) are all available in liquid form and do not pose the toxic inhalation threat that H₂S does.

The lowest lethal concentration published for CS₂ is 4000 ppm for 30 minutes. CS₂ is also used as an insecticide and when inhaled has an anesthetic effect resembling alcoholic intoxication. It is stable in air up to 194°F (90°C).⁽¹⁹⁾

DES has a characteristic garlic-like odor. No details are available on the toxicity of DES, but it is listed as "probably high." No details are available on fire hazard.(20)

Thiophene is a clear colorless liquid that is stable in air. The lowest published lethal concentration is 8700 ppm, for mice. The toxic summary for thiophene is listed as "moderate" via inhalation routes and "high" via intraperitoneal (or digestive) routes.(21) So if you smell it, be sure not to swallow.

Summary of MOCVD Sources for ZnS

The available physical data for sources used in growth of ZnS is summarized in Table 1. In general, liquid Zn sources are chosen when gaseous species are undesirable due to safety concerns. The advantage to gaseous Zn sources are that they can be metered more precisely since they are relatively insensitive to ambient temperature, etc. In the case of sulfur sources, H₂S is the most commonly used, but is a gaseous, highly toxic species that must be carefully managed. There are several desirable liquid species. DES, though, is expensive and requires high growth temperatures. CS₂ is less toxic and can be used in the 400°C growth temperature range.

Thiophene is less toxic than CS₂ but, according to Jones, et al.,⁽¹⁴⁾ requires growth temperatures around 450°C to 500°C.

In this work, DMZn in He is used as the zinc source and thiophene liquid with He as the carrier gas is used as the sulfur source.

<p>Table 1</p> <p>Physical Data for the Commonly Used Sources in the Growth of Zinc Sulfide</p>					
<u>Compound</u>	<u>MW</u>	<u>m.p.</u> <u>(°C)</u>	<u>b.p.</u> <u>(°C)</u>	<u>Forms Available</u>	<u>Ref.</u>
DEZn	123.49	-28.0	118.0	liq., gas mixture	(21)
DMZn	95.44	-42.2	46.0	liq., gas mixture	(22)
H ₂ S	34.08	-85.5	-60.7	gas, gas mixture	(17)
CS ₂	76.14	-111.5	46.2	liquid	(22)
DES	80.09	-103.8	92.1	liquid	(22)
C ₄ H ₄ S	84.14	-38.2	84.2	liquid	(22)

Kinetics of Reactions by MOCVD

An important factor in MOCVD growth is the dependence of growth rates on various parameters involved. Previous work has determined that as DMZn flow is

increased, the growth rate is increased. But in assessing the effect of DMZn flow rate, it is important to compensate for the changing carrier gas flow rate by altering the ballast gas flow rate so there will be no net change of flow rate into the reactor. With this pre-condition, the growth rate has been found by Yoshikawa⁽⁸⁾ to be directly related to the DMZn flow.

The temperature contribution on growth rate is also important to consider. In this case, it turns out that growth rate is directly related to temperature up to an optimum temperature, and above the optimum temperature, the growth rate is inversely related to the temperature. The reason for this is as follows: At low temperatures, it is the activation energy required for the deposition reaction that limits the growth rate. However, above the "optimum" temperature, desorption of reactants from the substrate begins to dominate the activation energy effect on growth rate, and if temperature is increased further, the growth rate will decline.

The dependence of growth rate on reactor pressure, holding flow rates fixed, was also studied by Yoshikawa⁽⁸⁾. They found that as the reactor pressure increases, the growth rate increases as well. But, at some saturation value, the effect on growth rate becomes negligible, and higher pressures will not change the growth rate.

II. Fabrication Techniques of Zinc Sulfide Devices

Greenberg, et al., grew epitaxial layers of ZnS on sapphire.⁽⁴⁾ They used CVD with sources of high purity ZnS and H₂ as the carrier gas. The growth temperatures they used ranged from 745°C to 870°C with a growth rate of 2.4 to 3.5 $\mu\text{m/hr}$ to achieve final thicknesses of about 15 μm .

Hirabayashi and Kogure⁽²³⁾ prepared thin film electroluminescent devices using the metal-insulator-semiconductor (MIS) structure. They began with a glass substrate covered with indium-tin-oxide (ITO), followed by a manganese-doped ZnS (ZnS:Mn) phosphor layer. Next, 0.35 μm of Sm₂O₃ was deposited by E-beam evaporation, and finally an aluminum electrode was evaporated on top. In their deposition of the ZnS layer they used dimethylzinc (DMZn) in a bubbler kept at -10°C with H₂ as the carrier gas. The sulfur source they chose was 5% hydrogen sulfide (H₂S) in hydrogen (H₂) gas. Growth was carried out at 300°C and at low pressure. The luminescence center Mn was introduced into the ZnS layer by thermal diffusion. This was chosen as an improvement over the doping method using tricarbonyl-methyl-cyclopentadienyl-Mn (TCM) because this needed to be carried out at ~450°C, leading to poor crystallinity of the ZnS layer, and reaction between the ZnS film and the ITO layer. The ZnS layer grown was

polycrystalline in nature, with individual grains of about 3500Å in diameter.

Another approach was chosen by Takata, et al.,⁽¹⁵⁾ who also worked on TFEL's. They used H₂ as a carrier gas bubbled through diethylzinc (DEZn) at 12°C and bubbled through carbon disulfide (CS₂) at -5°C. Growth temperature was varied from 200°C to 425°C, and was found to be optimum between 325°C and 425°C. Reactor pressure during growth ranged from 160 to 360 torr. This team was concerned about pre-reaction between the sources so they experimented with the CS₂ alone. Conducting a run while supplying only CS₂ + H₂ into the reaction chamber, they observed no deposition below 425°C. Then, supplying both CS₂ and DEZn with their respective carrier gases, they observed no ZnS deposit below 200°C. They found that with the growth temperature held at 400°C, the growth rate was linearly related to the S/Zn molar influx ratio. Also, they found that with a fixed S/Zn molar ratio of 20, that the growth rate was directly related to growth temperature up to 400°C, and that growth rate was inversely related to growth temperature above 400°C.

MOCVD-grown TFEL's using CS₂ have also been reported by Minami, et al.,⁽²⁴⁾ as a continuation of their work cited above.⁽¹⁵⁾ They used a barium titanate (BaTiO₃) ceramic sheet as both the insulating layer and substrate.

On top of this they deposited ZnS by MOCVD using DEZn and CS₂ at a S/Zn molar ratio of 20. They used growth temperatures ranging from 275°C to 400°C. Manganese for the luminescent center was thermally diffused into ZnS at 600°C in an argon atmosphere. The top electrode of aluminum-doped zinc oxide was deposited using radio frequency (rf) magnetron sputtering. Finally, an Al layer was evaporated onto the bottom of the ceramic sheet to serve as the back electrode.

Yet another approach to fabrication of TFEL devices is provided by Hirabayashi, et al.,⁽¹⁶⁾ who fabricated their devices using ZnS thin film layers obtained by photo-assisted MOCVD using dimethylzinc (DMZn) and diethyl sulfur (DES). Without photo-assisted growth, they reported a minimum growth temperature of 400°C, while with photo-assisted growth, they were able to reduce the minimum growth temperature to 300°C. The effect of photo-assisted deposition had two competing influences. On one hand, they were able to lower growth temperature, but on the other hand, the luminance of the photo-assisted prepared layers was lower due to irradiation damage causing many sulfur vacancies.

Finally, Migita, et al.⁽²⁵⁾ experimented with different Mn sources for doping the ZnS layer. MOCVD of ZnS was carried out using DEZn and H₂S and three different

Mn dopant sources: di- π -cyclopentadienyl manganese (CPM), bi-methylcyclopentadienyl manganese (BCPM), and tricarbonyl methylcyclopentadienyl manganese (TCM). In these studies, they found high efficiency and high luminance using either CPM or BCPM, but very low values when TCM was used. Other variables investigated were growth temperature ranging from 280°C to 350°C and reactor pressure ranging from 0.6 torr to 2.0 torr.

III. Apparatus

The MOCVD reactor used in this work is installed in the Materials Engineering Department at San Jose State University. It was first built by Marc Jensen⁽²⁶⁾ and modified by Hoa Do⁽²⁷⁾. Work has also been done using this system by Dennis Ramos⁽²⁸⁾, Hamid Kashani⁽²⁹⁾, Rex Chuang⁽³⁰⁾, and Richard Patten⁽³¹⁾. A schematic of this reactor is shown in Figure 10.

The reactor is designed for low pressure work, in the range of 0.5 to 10 torr. It is capable of using either liquid or gaseous sources of zinc and sulfur. Upon reaching the reactor, the sulfur source is injected at the end of the reactor tube and disperses throughout the chamber. The zinc source has two paths into the reaction chamber: (1) bypass, where the zinc flows outside the quartz liner in which the susceptor and substrate sit. Flowing the zinc through the bypass valve is useful for stabilizing flows and temperature before the onset of deposition, and (2) the inject valve, pointing directly at the susceptor where the zinc flows during the actual deposition of ZnS. To initiate and terminate growth, the zinc valve is toggled between the two states. Heating of the substrate is accomplished by two quartz lamps situated

on the bottom of the susceptor with output controlled by a VARIAC potentiometer.

Figure 10. MOCVD Apparatus.
Schematic of Low Pressure MOCVD Apparatus Used in
This Work⁽³⁰⁾.

Flow rates are controlled by needle valves located in the gas lines leading to the reactor and reactor pressure is set by a hand-operated vacuum valve which must be very carefully set to achieve the desired pressure. Temperature is sensed by two thermocouples, one situated above the susceptor, just behind the substrate, and the other situated along the underside of the susceptor, where the two heating lamps are located.

The mechanical pump used to exhaust the reactor is a 2-stage rotary vane pump with a capacity of 473 lit/min, ultimate pressure of 5×10^{-4} torr.

A burner unit is located downstream from the pump to burn the exhaust products. This unit is kept at 970°C to 1000°C during the runs. Inside the burner unit is some baffling to slow down the exhaust gases and ensure they are completely burned before they move into the scrubber.

The scrubber is a cylindrical stainless steel tank with two spray nozzles diametrically opposed and situated inside the tank at the top, aiming down at about a 45 degree angle. The exhaust gases enter the scrubber at the bottom and are sprayed down by the two nozzles. The heavier products are washed down the drain of the scrubber while the lighter products exit at the top of the scrubber into the building vent duct.

The entire gas handling portion of the reactor is located underneath a fume hood to minimize release of any toxic material into the room in the event of a leak.

The reaction that takes place at the susceptor is dependent on the reacting species being used. For example, if the species are DMZn and H₂S, the mechanism is fairly well understood and the deposition reaction has been found to be:

No mechanisms were found for the system of DMZn and thiophene (C₄H₄S), but one possibility is:

For this work, the zinc source used was 1% DMZn in helium and was metered into the reactor through a Matheson Model 603 rotameter. Both H₂S and thiophene were used for this work. 10% H₂S in helium was metered by a Matheson Model 602 rotameter. For the thiophene work, the H₂S line was disconnected and plugged, and the thiophene line was added in its place.

Substrate materials used were precleaned glass slides, and GaP substrates.

Actual flow rates were determined from the rotameter readout with the help of calibration charts from Hamid Kashani's work⁽²⁹⁾.

To determine actual thiophene flows, vapor pressure data of thiophene was used in combination with Kashani's calibration plots to determine actual concentration of thiophene in the gas stream.

The vapor pressure of thiophene is summarized in Table 2.

Table 2	
Vapor Pressure of Thiophene as a Function of Temperature ^(22,32)	
Pressure Temperature (mm Hg)	(°C)
1	-40.7
5	-20.8
10	-10.9
20	0.0
40	12.5
60	20.1
100	30.5
200	46.5
400	64.7
760	84.4

Using the information in Table 2, with the assumption that the bubbler is at approximately 1 atmosphere pressure and room temperature, the volume concentration of thiophene in helium reaching the reactor should be about $60/760 \times 100\%$ or about 8% thiophene in helium.

Actual operating procedures for running the MOCVD reactor are included in Appendix A.

IV. Procedures and Results for Thiophene

For the runs using thiophene, the H_2S line was disconnected upstream from the rotameter and plugged. A thiophene assembly was installed consisting of a plumbing line from a tank of pure He leading directly to the reactor. Branching off this line was a link which flowed through the thiophene bubbler, and then met right back up with the pure He line. A schematic of the thiophene assembly is shown below.

Figure 11. Schematic of thiophene line. Thiophene line used in the growth of ZnS by MOCVD. Note the three manually operated valves with which the direction of gas flow can be directed through the bubbler, or can bypass the bubbler and flow directly on to the reactor.

The thiophene line then continues on to the reactor.

Growths were carried out under the following range of conditions, also shown in Table 3:

[thiophene + He] flow rate	26-56 sccm
growth temperature	300-500°C
chamber pressure	1-10 torr

During some of these runs, especially at the higher growth temperatures, there was some carbonaceous material on the susceptor after deposition. There were, however, no ZnS deposits in any of the runs using the thiophene source.

The growth temperature limitation is one possible reason why ZnS deposition did not occur. Previous investigations^(15, 16) showed that the use of other sources, like DES and CS₂, required higher growth temperatures for deposition to occur. In the case of DES, the minimum growth temperature necessary, without photo-assist was 400° C, as shown in Figure 8. However, growth temperatures in the current work were taken as high as 500°C, still resulting in no deposit. It seems that some growth would have occurred if temperature were the dominating factor.

The pressure limitation is another possibility inhibiting the successful use of thiophene. The growth of ZnS by other researchers using sources other than H₂S has all been carried out at higher pressures. CS₂ was used at pressures ranging from 160-360 torr, and DES was used at a

pressure of 760 torr. The MOCVD reactor used for this work was designed for use at pressures in the range of 1-10 torr. It is possible that operating pressures are not high enough for the use of thiophene.

The work of Jones, et al.⁽¹⁴⁾ further reinforces the possibility that higher pressures are necessary for the use of thiophene. Their work was carried out at 760 torr.

In summary, a series of runs was carried out with thiophene, and although no growths resulted from that work, a likely reason for this is that higher operating pressures are needed for thiophene.

**Table 3. MOCVD of ZnS Run Data
using Thiophene as the Sulfur Source**

Run No.	Gr. Time (min)	Temp (C)	C ₄ H ₄ S		Tg (C)	Chamb. P (torr)	Comments
			Flow (sccm)	DH ₂ Flow (sccm)			
1	20	20	27	14	300	1	No ZnS
2	20	20	28	11	350	1	No ZnS
3	20	20	28	11	425	1	No ZnS
4	20	20	28	11	425	1	No ZnS
5	30	20	31	11	500	1	No ZnS, glass slide softening
6	30	20	27	11	375	1	No ZnS
7	30	20		11	325	1	Blown run, Thiophene not open
8	30	20	26	11	325	1	No ZnS
9	30	20	30	11	400	1	No ZnS
10	30	20	56	13	350	>1	No ZnS
11	30	20	56	10	350	>1	No ZnS
12	37	20	56	11	350	10	No ZnS
13							Blown Run
14	50	20	54	10	350	10	No ZnS

V. Procedures and Results for H₂S

After failing to get ZnS deposition using thiophene, the thiophene line was disconnected, and the H₂S line reattached. It was desired to obtain an idea of growth rate trends as a function of flow rate of H₂S and DMZn, and as a function of growth temperature. For evaluation of the runs using H₂S, a 2³ factorial design was used, resulting in eight runs for study of H₂S growth trends.

The data from these runs with the hydrogen sulfide reconnected is shown in Table 4.

For all the runs using H₂S, a cover slip was mounted on the substrate, positioned so that its edge would coincide with the estimated center of deposition. After growth, the cover slip was discarded and thickness measurements on the substrate were made using a Tencor Model 250 Thickness Profiler located at Hewlett-Packard. Several measurements were made searching for the point where thickness was greatest, indicating the center of deposition.

**Table 4. MOCVD of ZnS Run Data
using H₂S as the Sulfur Source**

Run No.	Gr. Time (min)	H ₂ S Flow (sccm)	DMZn Flow (sccm)	Tg (C)	Chamb. P (torr)	Thickness (μ m)	Gr. Rate (μ m/min)	Comments
15	20	29	9	300	6.4	8.4	0.42	
16	10	29	9	300	2.7	1.33	0.133	Good but spotty
17	10	16	10	250	2.7	2.42	0.242	Good, not spotty
18	10	16	10	350	2.7	2.26	0.226	Good dep.
19								Blown run
20	10	38	10	250	2.8	3.14	0.314	
21	10	38	10	350	2.8	5.27	0.527	
22	10	29	8	300	5	5.94	0.594	
23	10	16	8	250	3.86	3.62	0.362	
24	10	16	8	350	3.9	5.15	0.515	Good dep.
25	10	29	8	300	4.5	6.67	0.667	
26	10	38	8	250	4.1	6.64	0.664	
27	10	38	8	350	3.9	7.97	0.797	
28	10	38	8	250	1.6		0	Blown run
29	10	38	8	250	4.3	4.89	0.489	On GaP subst.
30	10	38	8	300	2		0	On GaP subst.
31								On GaP subst.
32	10	37	9	300	7.3	10.15	1.015	

Surface morphology was evaluated using an Olympus microscope equipped with Differential Interference Contrast (DIC) capability. The surface morphology was uniform in appearance, with a grainy texture and very little spottiness. Typical surface morphology on these wafers is shown in Figure 12. These micrographs were taken at 50x and 500x.

A cross-sectional photograph taken at 1500x magnification on a cleaved piece of run #29 on GaP substrate shows the polycrystalline nature of the layer in Figure 13. Finally, in Figure 14, a photo of an EDX spectrum confirms the presence of zinc sulfide.

Reproducibility of ZnS layers grown was also addressed. Run numbers 16, 22, and 25 were all grown at the same nominal temperature and flow rates. However, the pressure varied significantly in these three runs due to the difficulty of controlling pressure with a manually operated pressure control valve, and cannot be considered as a valid measure of reproducibility of thin films grown in this reactor.

The data points from Table 4 were manipulated into a series of graphs, each graph factoring out all but two variables. This series of graphs is shown in Figures 15-26. For instance, in Figure 15, of the three parameters

studied affecting growth rate, H_2S flow, DMZn flow, and growth temperature, data points were chosen with the growth temperature fixed at $250^\circ C$. There are two data lines in Figure 15. One corresponds to DMZn flow fixed at 8 sccm, and the other corresponds to DMZn flow at 10 sccm. Once these variables are factored out, the remaining two variables, H_2S flow and thin film thickness were plotted against one another. So in summary, Figures 15 through 18 examine film thickness versus sulfur flow with different combinations of the other two variables held constant, Figures 19-22 show film thickness versus DMZn flow, and Figures 23-26 show film thickness versus growth temperature. All of these growths were 10 minutes in duration, so the extensive variable growth time was plotted in place of the intensive variable growth rate in all of these graphs.

The graphs shown in Figures 15-26 suggest trends in what influences the growth rate. For example in Figures 15-18, every data line shows an increase in growth rate when the H_2S is increased.

The next four figures, Figures 19-22, show a decrease in growth rate with an increase in DMZn, which is a little harder to explain. A key for the reason to this may be found in the work by Yoshikawa⁽⁸⁾. In his work, when he was evaluating the effect of [DMZn + He] flow on growth

rate of ZnS, he was able to compensate for an increase in the [DMZn + He] flow by reducing the flow of the ballast He by an equal amount. He was, in this way, able to increase the amount of zinc precursor delivered to the reactor, but at the same time keep constant the sum of all flows into the reactor to achieve a true evaluation of the dependence of flow of DMZn on the growth rate.

In the case of San Jose State's MOCVD reactor, such an evaluation was not possible. In Figures 19-22 which show the effect of growth rate on DMZn flow, the total flow into the reactor is increasing when the [DMZn + He] flow is increased. This leads to the possibility that there is actually a geometric effect reducing the growth rate with increasing [DMZn + He] flow. Since the DMZn that enters the reactor enters just above and flowing directly toward the substrate, it is likely that increasing its flow is inhibiting the flow of H₂S to the substrate. This would naturally cause a reduction of the growth rate as the amount of a stoichiometric mix of zinc and sulfur has been reduced by raising the [DMZn + He] flow.

Figures 23-26 show film thickness as a function of growth temperature. Once again, these four figures show a direct relationship between film thickness and growth temperature. However, if this evaluation was carried out over a broader range, there should be a temperature where

growth rate will be maximized, and above this temperature an inverse relationship will be exhibited. This is due to the increasing effect of desorption of reactants from the substrate as temperature is increased.

Figure 12. Surface Morphology of ZnS.

Optical micrographs of run BP-15 which was ZnS using H_2S and grown on a glass slide. The left micrographs was taken at 50x and the right micrograph was taken at 500x.

Figure 13. Cross Section of ZnS.

Optical micrograph taken of cross-section of ZnS grown on gallium phosphide showing the polycrystalline nature of the thin film. This micrograph is from BP-29 and was taken at 1500x magnification.

Figure 14. Energy Dispersive X-Ray of ZnS.
Energy dispersive X-ray of ZnS grown on GaP, confirming that the thin film is actually ZnS. Sample was from run BP-29.

Figure 15
Thickness vs. Sulfur Flow
At T=250C

Figure 16

Thickness vs. Sulfur Flow

At T = 350 C

Figure 17
Thickness vs. Sulfur Flow

Figure 18

Thickness vs. Sulfur Flow

At DMZn flow = 10 sccm

Figure 19
Thickness vs. DMZn Flow
At T=250°C

Figure 20

Thickness vs. DMZn Flow

At T = 350 C

Figure 21

Thickness vs. DMZn Flow

AlH₂SFlow=16 sccm

Figure 22

Thickness vs. DMZn Flow

At H₂S Flow = 38 sccm

Figure 23

Thickness vs Growth Temp.

At DMZn Flow = 8 sccm

Figure 24
Thickness vs Growth Temp.

Figure 25

Thickness vs. Growth Temp.

Al H₂S Flow = 16 sccm

Figure 26

Thickness vs. Growth Temp.

At H₂S Flow = 38 sccm

VI. Conclusion

Use of thiophene in this reactor is not feasible at present. A recommendation would be to try a different liquid sulfur source such as carbon disulfide for which lower growth temperatures have been reported than for thiophene and DES. But first it would be better to modify the reactor to operate at higher pressures. The present 10-15 torr maximum just isn't high enough for any sulfur source but H_2S .

Very good growth rates are obtainable with the use of H_2S , and the reactor is well suited for use in the optimum range of this source.

The data obtained from using the H_2S showed that the growth rate was directly related to the $[H_2S + He]$ flow and to growth temperature. However, there was an apparent inverse relationship between $[DMZn + He]$ flow and growth rate. This was due to the fact that increasing the DMZn flow unavoidably increased the flow of its carrier gas and inhibited the ability of H_2S to reach the substrate and react with the DMZn.

Surface morphology of the runs using H_2S overall had a uniform grainy appearance and thickness of the layers had a more or less radial distribution.

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VI. Appendix
MOCVD Operating Procedures

MOCVD OPERATING PROCEDURES

- I. Turning the H₂S toxic detector on.
 - Pull pin out of the top of the meter (unit will start beeping).
 - Hit alarm button (beeping should go off).
- II. Turning on the power to the control panel.
 - Flip up main breaker, turn on "power" on the left side of the control panel.
 - Turn on burner switch on control panel (to the right of the power switch). Let warm up about one minute.
 - Open yellow valve on wall behind the gas box which is at about eye height. This turns on the scrubber water.
 - Open air to burner valve (red tube hanging down above MOCVD control panel) slightly. Check for flow by disconnecting at union above the gas cabinet. There should be a low flow. Reconnect union.
 - Flip on burner VARIAC power switch and set output initially at 10. Increment output slowly up to 110 during the start-up process.
 - Check for draw in gas cabinet (use a piece of paper to test flow).

- Use toxic detector to check for H_2S presence in gas cabinet.
- Increment burner output a little more.
Ultimately, you want 1000°C corresponding to a VARIAC output of about 110.

III. Bringing chamber up to atmosphere for substrate loading/unloading:

- Open N_2 cylinder valve (don't change regulator pressure--make sure it's left at 15 psi).
- Press V3 (N_2 valve) on front panel. This starts N_2 flow into the reactor.
- Watch vacuum gauge on top of reactor chamber.
When at 1 atm, pull out susceptor.
- Disconnect thermocouples at susceptor holder.
- Unplug heater power cord.
- Bring out susceptor.
- Load substrate.
- Turn on mechanical pump (front panel).
- Flip vac-to-air valve off (down position).
- Insert susceptor back into the chamber and close.
- Open hand vac valve to draw vacuum.
- Turn off Valve 3 on Control panel.
- Reconnect thermocouple. On chamber door, the upper TC port measures at the susceptor, and the lower TC port measures below the susceptor.

Note: On back of MOCVD control panel, only the top thermocouple wire works, so use only that one and plug into the desired TC port on the reactor chamber door.

- Reconnect heater power cord.

IV. Evacuating chamber and stabilizing at low pressure.

- Open the hand vacuum valve to begin pump down.
- When the pressure reaches about 40 microns, turn on V3 valve to allow N_2 to flow for about 5 seconds.
- Turn off V3 and allow to pump back down to 40 microns.
- Repeat above two steps twice more.
- During the third and final pump down, when the pressure reaches 40 microns, close hand vacuum valve and continue with next section.

V. Heating up the system.

- Turn on substrate VARIAC on top of table.
- Increase output slowly by increasing by 10 every few minutes. Ultimately want output at about 50% which corresponds to about 300°C using Set I on Athena temperature controller.

Note: If fuse on VARIAC burns out, ask Jack in EE. His office is across from EE department office on the third floor of the engineering building.

Rex has gone as high as 400°C using:

Variac output at 60%

But at low pressure of 10^{-6} torr.

At 1 mtorr and 60% output would probably have
T=430°C.

The thermocouple measures susceptor temperature, not
substrate temperature. So Rex adjusts the TC to about
301-302°C at susceptor. Then substrate should be right
about 300°C.

Probably need to make small adjustments in VARIAC
fairly often to keep at setpoint temperature.

-- Now wait 20-30 minutes until set temperatures have
been reached

<u>Variac</u>	<u>Output</u>	<u>Temp</u>
Substrate	50%	300°C
Burner	115	970-1000°C

Note: If burner valve is not heating up to
1000°F, turn down air-to-burner flow (red valve) a
little.

-- Can speed up susceptor heat-up by letting in small
burst of N₂, and then open hand vacuum valve to
achieve a little lower pressure, then close hand
vacuum valve.

V. Setting up the source gases.

- Open H₂S cylinder valve and valve leading out of the gasbox.
- Open DMZn cylinder valve and valve leading out of the gasbox.
- Flip open Valve 10/11 toggle switch on back of control panel.
- Open V1 (DMZn) and V2 (H₂S) needle valves.
- Open hand vacuum valve slightly before the next step.
- Depress buttons labeled "1" and "5" on control panel. This introduces H₂S into the reactor chamber and DMZn to bypass. Now will need to adjust hand vac valve to reach 1 mtorr chamber pressure.

VI. Stabilizing flows and commencing deposition.

- Make sure the pressures, flows, and temperatures are at the desired setpoints.
 - Stabilize pressures and flow rates by setting rotameters to the desired flow, and then adjusting chamber pressure to 1 mtorr using the hand operated vacuum valve above the reaction chamber.
- Typical rotameter settings are as follows:

<u>Valve</u>	<u>Gas</u>	<u>Black/Silver</u>
V1	DMZn	13/6
V2	H ₂ S	44/15.5

- Let stabilize for 20 minutes.

- Switch "1" off and "2" on to introduce DMZn into the reactor chamber and begin deposition.
- Typical deposit time is about 10 minutes.

VII. After deposition:

- On control panel, turn off "2" and turn on "1" which sends DMZn back to bypass. Let susceptor cool down with H₂S still flowing.
- When susceptor temperature reached 150°C, turn off "1" and "5" which turns off H₂S and DMZn flow.
- Pressure will start to drop. Now need to cycle N₂ through the chamber to clean out toxic gases and help cool the substrate:
 1. When pressure reaches 20-30 microns, turn on V3 on control panel.
 2. Open vacuum valve more so pressure doesn't reach atmosphere, and also to purge out toxic gases.
 3. Wait for 5 minutes.
 4. Turn off V3.
 5. Repeat steps 1-4 two more times.
- Turn off substrate VARIAC by turning output back to zero and then flipping off the toggle switch.
- Close V2, V1 needle valves.
- Flip off 10/11 toggle switch on back of MOCVD control panel.

- Shut off H_2S and $DMZn$ cylinders in the gas cabinet.
- Let susceptor cool to $100^{\circ}C$.
- Allow the chamber to come up to atmosphere one last time. When vacuum gauge on top of reactor chamber reads 1 atmosphere, susceptor can be unloaded. Don't forget to unplug the electrical cord and the thermocouples before pulling out the susceptor.
- Unload the wafer.
- Put substrate holder back in chamber while opening hand operated vacuum valve.
- Turn off $V3 N_2$ valve.
- Wait for pressure to reach 30-40 microns.
- Close hand vacuum valve all the way.
- Close the two N_2 cylinder valves.
- Turn off burner variac.
- Turn off burner switch on the control panel.
- Flip up (open) vac-to-air valve.
- Turn off mechanical pump switch on control panel.
- Turn off power supply and turn off main breaker on control panel.
- Shut off water (yellow valve) and air (red hose).
- Make sure H_2S detector is back in its box with plug in place.