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CHEMICAL VAPOR DEPOSITION OF IR MATERIALS

S. R. Steele

J. Pappis

Raytheon Company
Research Division

Technical Report AFAL-TR-71-200

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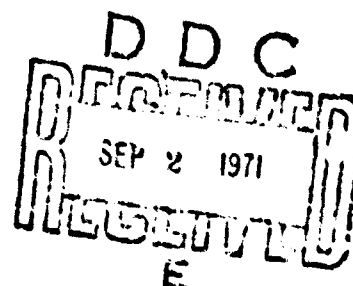
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Air Force Systems Command

Wright-Patterson Air Force Base, Ohio 45433



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The feasibility of fabricating infrared optical materials with high transmissivity in the 8 to 14 micrometer region of the spectrum by the chemical vapor deposition process was demonstrated by depositing small plates of both zinc and cadmium sulfide. 2 X 4 X 1/4 in. prototype samples were fabricated of zinc sulfide, an economical material satisfying most of the goals of this program. Two of these prototype samples were delivered after validating measurements showed them to have a transmittance in excess of 60 percent from 6 to 12-1/2 micrometers, a flexural strength of 11,000 psi, and a use limit above 200 °C. A 1 X 2 X 3/16 in. CVD cadmium sulfide sample was made which showed a transmissivity of over 60 percent from 2.5 to 14 micrometers. CVD CdS gave average flexural strengths up to 7800 psi, and small angle scattering as low as one milliradian. The potential for scaling to larger sizes was demonstrated by making 6 X 12 X 1/8 in. CVD zinc sulfide plates. No impurity absorptions were found in any of the CVD zinc sulfide or cadmium sulfide materials.		

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**CHEMICAL VAPOR DEPOSITION
OF IR MATERIALS**

**S. R. Steele
J. Pappis**

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FOREWORD

This report was prepared by Raytheon Company, Research Division, Waltham, Mass., under Contract No. F33615-70-C-1577, Project No. 4056, Task 01, entitled, "Chemical Vapor Deposition of IR Materials." The work was administered under the direction of the Air Force Avionics Laboratory, Wright-Patterson Air Force Base, Ohio. Mr. C. T. Ennis (RSO-3) was task engineer.

At Raytheon, the investigation was carried on in the Advanced Materials Department of the Research Division. Dr. J. Pappis is Department Manager, and Mr. S. R. Steele, principal investigator.

This is the Final Technical Report for Contract F33615-70-C-1577. It covers the period May, 1970 to June, 1971.

This report was submitted by the authors June, 1971.

This technical report has been reviewed and is approved.



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ABSTRACT

The significance of this research and development to the Air Force is the demonstrated feasibility of fabricating large infrared transmitting windows with good physical characteristics. The chemical vapor deposition (CVD) process used in this demonstration is not severely size or shape limited. The CVD process has the potential of fabricating 1 ft. X 2 ft., 8 to 14 micrometer transmitting IR optical windows, pyramidal and 180 degree domes. 2 X 4 X 1/4 in. prototype samples were fabricated of zinc sulfide, an economical material satisfying most of the goals of this program. Two of these prototype samples were delivered after validating measurements showed them to have a transmittance in excess of 60 percent from 6 to 12.5 micrometers, a flexural strength of 11,000 psi, and a use limit above 200° C. A 1 X 2 X 3/16 in. CVD cadmium sulfide sample was made which showed a transmissivity of over 60 percent from 2.5 to 14 micrometers. CVD CdS gave average flexural strengths up to 7800 psi, and small angle scattering as low as one milliradian. The potential for scaling to larger sizes was demonstrated by making 6 X 12 X 1/8 in. CVD zinc sulfide plates. No impurity absorptions were found in any of the CVD zinc sulfide or cadmium sulfide materials.

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SECTION I

INTRODUCTION

Reconnaissance and weapon delivery applications require infrared windows that can be fabricated in large sizes and various shapes. A considerable effort has been devoted over the past decade toward the development of suitable windows. Window blanks in general have been formed by special glass casting, hot pressing, and crystal growth techniques, but none of these are totally satisfactory. Some of the more common problems encountered with windows formed by these processes are: size limitations, nonuniformity of transmissivity and refractivity, impurity absorptions, and high cost.

The chemical vapor deposition (CVD) process is not inherently size limited and it has the potential of fabricating polycrystalline infrared transmitting materials. The Air Force, recognizing the potential of CVD for fabricating large aperture infrared windows, initiated a program at Raytheon whose objectives were: 1) To investigate the feasibility of utilizing the CVD process to fabricate materials that exhibit a transmissivity of 60 percent or greater in the 8 to 14 micrometer region of the spectrum, and 2) to determine feasibility of scaling the CVD process to fabricate infrared transmitting materials in large sizes.

Raytheon's approach has been: 1) Make exploratory depositions of zinc sulfide, a material which can be economically and safely

handled and whose properties satisfy most of the goals of this program, 2) once adequate control of the process has been achieved, make $2 \times 4 \times 1/4$ inch samples of CVD zinc sulfide, validate their properties and deliver them to the government, 3) prove the general utility of the CVD process for IR window fabrication by fabricating and evaluating CVD cadmium sulfide, and 4) make experimental depositions of zinc sulfide in large mandrels to prove the feasibility of scaling.

SECTION II

THE CHEMICAL VAPOR DEPOSITION PROCESS

In the CVD process, volatile compounds of the elements composing the material to be deposited are reacted at a surface whose temperature allows the compound to decompose or react to form a solid, adherent layer. The volatile byproducts of the reaction can be pumped away, flushed away in a stream of carrier gas, removed by reaction with a mass of some suitable material in the system, or regenerated and reused by reaction with a reservoir of a suitable raw material.

Chemical vapor deposition processes can be used to form the most refractory substances at temperatures where their vapor pressures are negligible. The properties of chemical vapor deposited materials can be significantly and controllably altered by the co-deposition of alloying atoms. Depending upon the relative concentrations of the reactants, either solid solutions or two-phase composites can be formed. Crystallite orientation and size distribution can be controlled by proper manipulation of the deposition parameters. Composites with alternating layers or two or more different materials can be prepared by cycling the composition of the vapors from which the materials are deposited.

Two general types of systems, static and dynamic, can be used for chemical vapor deposition. The static system is a closed system; in which the reactants and products are sealed in a chamber. Well-known examples are the quartz-iodine incandescent lamp and the hydrothermal bomb for the deposition of synthetic quartz. In the dynamic system, fresh reactants are continuously metered into the deposition chamber, and the spent vapors are continuously removed, usually by pumping. Figure 1 is an example of a simple dynamic CVD system. The reactive gases are fed into the furnace through a gas-metering system. The substrate upon which the deposit occurs is maintained at an appropriate temperature by means of a heater that is inductively or resistively heated. Most vapor depositions are made at pressures on the order of one-hundredth of an atmosphere, although a much higher or lower pressure can be employed. The dynamic system is used for the deposition of most materials, particularly when large shapes are to be made.

Two general techniques can be employed in vapor deposition. These are: (1) Conventional chemical vapor deposition where the vapor source temperature is lower than the substrate temperature; (2) Transport chemical vapor deposition, where the vapor source temperature is higher than the substrate temperature. Depending upon the nature of the chemical reactions involved, it is possible to utilize either technique in a static or a dynamic system. In conventional chemical vapor deposition, the thermodynamics and kinetics of the chemical reactions

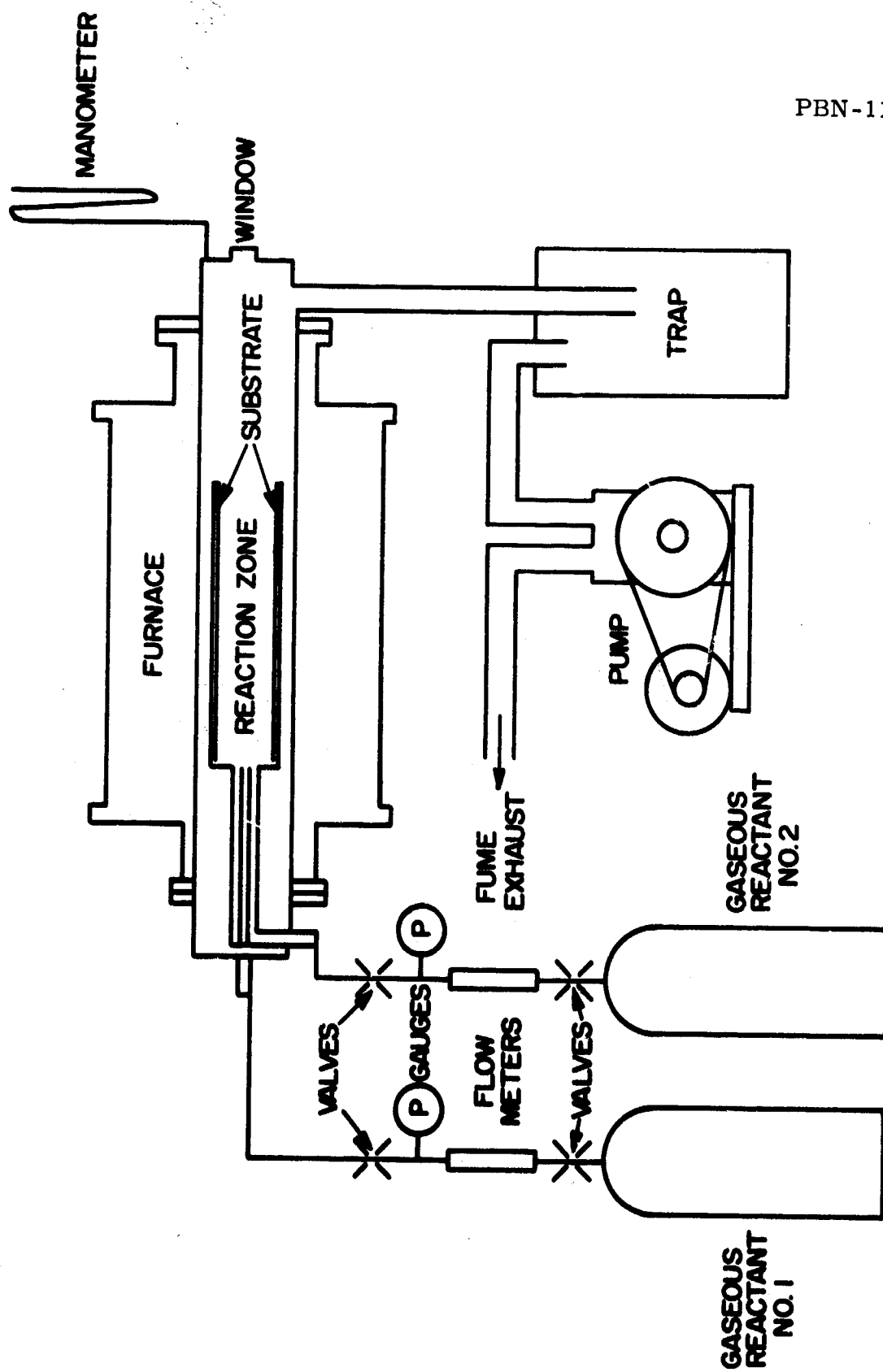


Fig 1 Schematic of Typical Dynamic CVD System

are such that formation of the solid product is favored at the higher temperatures, whereas the volatile reactants tend to be formed or are stable at the lower temperatures. In chemical transport deposition, on the other hand, the thermodynamics and kinetics of the chemical reactions are such that formation of the solid product is favored at the lower temperatures, whereas the volatile reactants are formed at the higher temperatures. Both techniques were tried in a dynamic system in exploratory depositions of zinc sulfide. The conventional vapor technique yielded superior results.

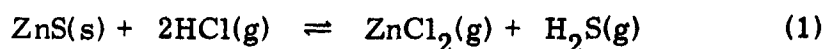
SECTION III

TRANSPORT CVD OF ZINC SULFIDE

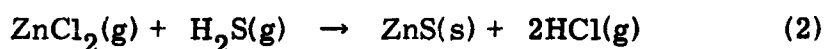
Considerable success has been reported for the growth of single crystals of zinc and cadmium sulfides, tellurides, and selenides by transport chemical vapor deposition using halogens or hydrogen halides as the transporting agent.⁽¹⁾ This method is attractive because:

- a) The raw materials are economical. Solid zinc selenide, for example, is much cheaper than hydrogen selenide gas.
- b) The reactive vapors are automatically generated in stoichiometric proportion
- c) No highly toxic gases are handled. All toxic chalcogenides remain non-volatile until they are heated in the closed retort.

For these reasons the early attempts to deposit zinc sulfide on this program were made using the transport CVD technique in a dynamic system. Dry hydrogen chloride gas was passed over high-purity zinc sulfide powder in a heated retort to generate zinc chloride vapor, hydrogen sulfide gas, together with unreacted excess hydrogen chloride gas in accordance with the following reversible reaction:



A fairly large flow of helium was added as a diluent to improve the transport efficiency and to make the deposition rate more uniform over the substrate. The vapors generated in the retort were transported downstream where they were directed over a substrate whose temperature was held well below that of the retort, where the reverse reaction occurred:



Equilibrium constants for these reactions are available in the literature.² These indicate that reaction (1) above is favored at high temperature and reaction (2) at low temperature. In a dynamic system, however, equilibrium is not apt to be attained and calculations based on equilibrium constants can serve only as a guide.

Experimentally it was found that the transport efficiency (measured as the fraction of zinc transported from the retort, of that which would be transported if reaction (1) were completely efficient) ranged from 15% at a retort temperature of 1025° C to 46% at a retort temperature of 1225° C. This meant that even at 1225° C about half the HCl gas remained unreacted and flowed downstream over the substrate and reacted with the deposited ZnS. It was found necessary

to add excess H_2S at the mandrel in order to obtain reasonable deposition efficiencies.

Initially, one of Raytheon's standard 4 in. diameter chemical vapor deposition systems was modified to make it more suitable for the exploratory depositions of zinc sulfide. A closed-end fused silica tube 3 in. dia. by 29 in. long served as the inner chamber of a double vacuum system, while the original 4 in. dia. system served as the outer chamber. The two chambers were independently pumped, the outer chamber with a mechanical pump, the inner with a trapped diffusion pump.

After the first few runs, it became obvious that a sharp temperature gradient was desirable between the retort zone held at 1000° to 1200°C and the substrate zone held at 700° to 900°C . It was not possible to provide this in a standard furnace; therefore a special two-zone furnace was constructed. The deposition chamber itself was a 4 ft. length of mullite tubing 3-1/2 in. i.d. surrounded by two heaters, one of which provided a 6 in. long uniform high-temperature zone for the retort, while the other provided an 8 to 10 in. long uniform low-temperature zone for the substrate. A 1-1/2 in. gap between the two heaters resulted in a sharp temperature gradient between the hotter retort zone and the cooler substrate zone.

Three cold traps in series followed the deposition chamber. These were kept filled with dry ice and acetone during the deposition in order to trap water vapor and sulfur without trapping excess HCl and H₂S. The latter two vapors were trapped by KOH traps. During heatup and prior to deposition, the valve to the KOH traps remained closed and the system was outgassed on the auxiliary pumping system. Approximately 30 min. before the deposition began, argon flows were established through retort and furnace, and the valve through the KOH traps was opened. At the beginning of deposition the desired dry HCl and H₂S gas flows were established and deposition proceeded.

Considerable difficulty was experienced with sulfur deposits which accumulated at constrictions in the exhaust system. These restricted pumping speed so that several runs had to be terminated prematurely when it became impossible to maintain a constant deposition pressure. This problem was finally overcome by eliminating all constrictions which might serve as potential trouble spots.

A second limitation was the small capacity of the retort holding the zinc sulfide reactant. Originally this was an alumina tube, both ends open 1-1/2 in. dia. by 12 in. long which held a charge of 100 to 200 grams of zinc sulfide powder. A ceramic disc, perforated with many 0.1 mm dia. holes, and backed with a quartz wool pad, was secured in the tube 1 in. from the end nearest the substrate. This

served as a filter, retaining the powder, while allowing the vapor to pass. The retort tube was sealed with a Viton O-ring to a water-cooled flange at the gas inlet.

Later a reservoir holding 1500 grams of loose powder was built. The reservoir, which was held at room temperature, was attached to a cylindrical tube through which a plunger could be driven into the hot retort. In principle, the charge of zinc sulfide powder in the retort could be replenished periodically during the run by activating the plunger.

Two fairly long deposition runs were made using this system. The plunger was modified in the second run to overcome sticking problems experienced in the first run. For both runs the zinc sulfide powder was prefired in vacuum at 900° to 1000°C for one hour to increase particle size and make it flow more freely. The replenishment system functioned satisfactorily, and although some difficulties in feeding were encountered, these could have been overcome by a redesign of the plunger system. However, the grain size of the resulting deposit was still too large. The question arose as to whether some powder was blowing out of the retort as a result of the replenishment operation.

To check this, and still make a fairly thick deposit, the ZnS powder was isostatically pressed into a cylindrical shape just the right

size to fit into the retort. In this way 360 grams of ZnS could be accommodated by the retort. The resulting materials still displayed about the same grain size.

Deposition rates in transport CVD ranged from 3 to 15 thousandths of an inch per hour. The actual deposition rate obtained depended somewhat upon pressure, flow conditions, and position in the mandrel. The strongest dependence, however, was upon the temperature difference between retort and mandrel. The highest deposition rate was usually obtained when the mandrel was about 200°C cooler than the retort, regardless of the absolute temperatures of either.

Several grades of zinc sulfide were used to charge the retort. In the initial runs, used to obtain a fix on the process conditions, 99.9 percent zinc sulfide powder was used for economy. In later runs 99.9 and 99.999 percent powder was used. Based on infrared scans, the purity of the deposited material seemed to depend strongly on the purity of the zinc sulfide powder used.

A total of twenty depositions of ZnS were made using transport CVD (see Table I) without obtaining satisfactory material. The most severe problem experienced was the inability to reduce the crystallite size sufficiently to obtain adequate mechanical and optical properties without adversely affecting density or purity. Four parameters were

TABLE I

EXPLORATORY ZINC SULFIDE DEPOSITIONS
(Transport CVD)

Run No.	Retort Temp. (°C)	Substrate Temp. (°C)	Pressure (torr)	HCl	Gas Flows (cc/min) He	H ₂ S	Reactant in Retort	Transport Rate (g/hr)	Substrate Material
ZS-1	850	700	380	160	500	60	ZnS	1.6	fused silica
ZS-2	1050	600 to 900	380	160	500	60	ZnS	2.5	fused silica
ZS-3	1050	600 to 900	380	320	1500	320	ZnS	6.1	fused silica
ZS-4	1050	600 to 900	760	320	1500	320	ZnS	6.4	fused silica
ZS-5	1000	750	760	320	2000	320	ZnS	*	graphite
ZS-6	1050	780 to 820	400	320	2000	320	ZnS	2.0	alumina
ZS-7	Abort	---	---	---	---	---	---	---	---
ZS-8	1020	740	450	320	2000	320	ZnS	11.5	alumina
ZS-9	1110	700	420	320	2000	320	ZnS	2.0	PG
ZS-10	Abort	---	---	---	---	---	---	---	PG
ZS-11	1150	730	420	320	2000	320	ZnS	6.5	PG
ZS-12	1200	700	90	320	2000	320	ZnS	19.0	PG
ZS-13	Furnace Tube Failed							---	---
ZS-14	1100	720	55	320	2000**	320	ZnS	13.0	PG
ZS-15	1100	720	75	320	3000	160	ZnS	15.0	PG
ZS-16	1100	720	45	320	3000	100	ZnS	15.0	PG
ZS-17	1150	720	50	420	3000	60	ZnS	20.0	PG
ZS-18	1150	710	50	420	3000	100	ZnS	12.0	glazed Al ₂ O ₃
ZS-19	1150	725	50	420	3000	100	ZnS	21.0	silica/glaz. alum.
ZS-20	1150	730	50	420	3000	100	ZnS	14.0	glazed alumina

* Not measured, burned out retort heater.

** Last run in which helium was used. Argon used in remaining runs.

varied: 1) The deposition pressure was lowered stepwise from 400 torr to 50 torr, 2) The substrate temperature was lowered stepwise from 800° to 650°C, 3) The H₂S flow was varied between 320 cc/min. to 60 cc/min., 4) The argon flow was increased from 2 lpm to 3 lpm. These steps finally resulted in a much smaller crystallite size than was obtained in the first runs, but they were still too large.

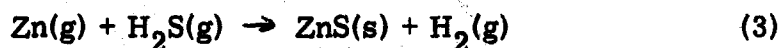
It was concluded that larger-than-desired grain size was inherent to the method. Excess HCl is always present in the vapor stream. This HCl increased the mobility of the zinc and sulfur atoms at the substrate, encouraging atomic rearrangement and crystal growth of the zinc sulfide, resulting in excessively large grain size. At higher retort temperatures a larger fraction of the HCl is used. For these reasons the retort temperature was made as high as possible (about 1200°C) but, even so, some unreacted HCl remained in the reactive gases in the deposition zone, encouraging grain growth. In addition, microprobe analyses showed that a small amount of chlorine remained in solution in the deposited zinc sulfide. Whether this retained chlorine would have adverse effects on infrared transmission has not been determined but the deposits were greenish when viewed by visible light. In any event it seemed desirable to reduce or eliminate the HCl from the system. This could not be done using transport CVD.

SECTION IV

CONVENTIONAL CVD OF ZINC SULFIDE - EXPLORATORY

The experiments described in the previous section resulted in CVD ZnS with a large grain size. This was attributed to the use of halogens or hydrogen halides which allowed the zinc and sulfur atoms to have high mobility at the substrate. This defect appeared to be inherent to transport CVD; therefore it was decided to try conventional CVD.

A reaction which can be used is:



Zinc has a vapor pressure of 40 torr at 673°C (Table II), and the dissociation pressure of ZnS is about 1.4×10^{-14} at the same temperature (Table III). Hydrogen sulfide is gaseous and is about 1 percent dissociated at 673°C. Thus, all the ingredients of a successful vapor deposition process are available provided the kinetics of reaction (3) are suitable.

Four exploratory conventional CVD runs were made in the same small system used earlier for transport CVD of zinc sulfide (Table IV). Zinc pellets (99.999 percent pure) were placed in the

TABLE II

**SOME THERMOCHEMICAL DATA RELEVANT TO THE VAPOR DEPOSITION
OF METAL CHALCOGENIDES**

A.		Heat of Melting (kCal/ mole)		Temperature at Given Vapor Pressure (torr)					Heat of Vaporization (kCal/ mole)		
Elements	MP (° C)			1	10	40	100	400	BP		
Zn	420		1.77	487	593	673	736	844	908	27.6	
Cd	321		1.45	394	484	553	611	711	765	23.9	
S	119		0.34	184	244	288	327	400	445	2.3	
Se	217		1.3	356	442	506	554	637	685	6.3	
Te	450		4.18	520	650	753	838	997	1087	12.1	
Cl ₂	-101		1.63	-118	-101	-85	-72	-47	-34		
Br ₂	-7		1.56	-49	-25	-8	+9	41	58	7.0	
I ₂	113		2.81	39	73	97	117	160	183	6.3	
B.		Heat of Formation (kCal/ mole)		Entropy (° Cal/ mole)		Log K _P at MP (atm ³)		P _{min} at MP (atm)		T° C at given P _{min} 15 torr 1.5 torr	
Compounds	MP (° C)										
ZnS	1830		49		14	0.85		3.7	1242	1082	
ZnSe	1520		39		20	-1.65		0.5	1224	1065	
ZnTe	1295		26		22	-1.4		0.6	1017	893	
CdS	1475		38		17	0.9		3.8	1015	890	
CdSe	1239		32		23	-2.0		0.4	1002	880	
CdTe	1092		24		23	-2.7		0.2	910	790	

Table II (Cont'd)

C.	Volatile Compounds	MP (° C)	Temperature at Given Vapor Pressure (torr)					BP
			1	10	40	100	400	
	ZnCl ₂	365	428	508	566	610	689	732
	CdCl ₂	568	566	656	736	797	908	967
	ZnI ₂	446	386	467	526	571	648	689
	CdI ₂	385	416	512	584	640	742	796
	ZnF ₂	872	1243	1359	1448	1527	1690	1770
	CdF ₂	520	1385	1559	1673	1759	1924	2024
	H ₂ Se	-64	-115	-98	-85	-74	-54	-41
	H ₂ S	-85	-134	-116	-102	-92	-72	-60
	H ₂ Te	-49	-96	-75	-59	-46	-17	-2

TABLE III
DISSOCIATION PRESSURES OF ZnS AND CdS

Minimum Dissociation Pressure (torr)	Cadmium Sulfide (°C)	Zinc Sulfide (°C)
14	1001	1242
1.4	876	1078
1.4×10^{-1}	769	954
1.4×10^{-2}	679	844
1.4×10^{-3}	604	758
1.4×10^{-4}	540	675
1.4×10^{-5}	497	608

TABLE IV

EXPLORATORY ZINC SULFIDE DEPOSITIONS
(Conventional CVD)

Run No.	Retort Temp (°C)	Substrate Temp (°C)	Pressure (torr)	Gas Flows (cc/min)		Reactant in Retort	Reactant Transport Rate (g/hr)	Substrate Material
				A	H ₂ S			
ZS-21	660	710	40	3000	320	Zn compd.	17.5	Al ₂ O ₃
ZS-22	710	710	40	3000	320	Zn "	22.0	Al ₂ O ₃
ZS-23	735	710	100	3000	320	Zn "	27.6	SiO ₂ & PG
ZS-24	750	750	100	3000	640	Zn "	35.0	PG

retort which was heated to temperatures between 650° and 750°C. Argon (99.995 percent pure) was flowed through the retort as a carrier gas. The zinc flow over the substrate was controlled by controlling the argon flow and the zinc retort temperature. Hydrogen sulfide gas (99.5 percent pure) was flowed through a separate inlet over the mandrel.

The first run of this series (ZS-21) yielded material which was much finer grained than had been obtained in any of the twenty runs made using transport CVD. The second run (ZS-22) produced an intact cylinder 22 in. long $\times$ 3 in. in dia. by .06 in. thick. The third (ZS-23) and fourth (ZS-24) produced 1 X 4 X 1/8 in. plates.

The infrared transmissivity of run ZS-23 was comparable to commercially available hot pressed zinc sulfide that is used for infrared windows (Fig. 2), although the internal scattering was somewhat greater.

The flexural strength (Table V) was also comparable to the hot pressed material.

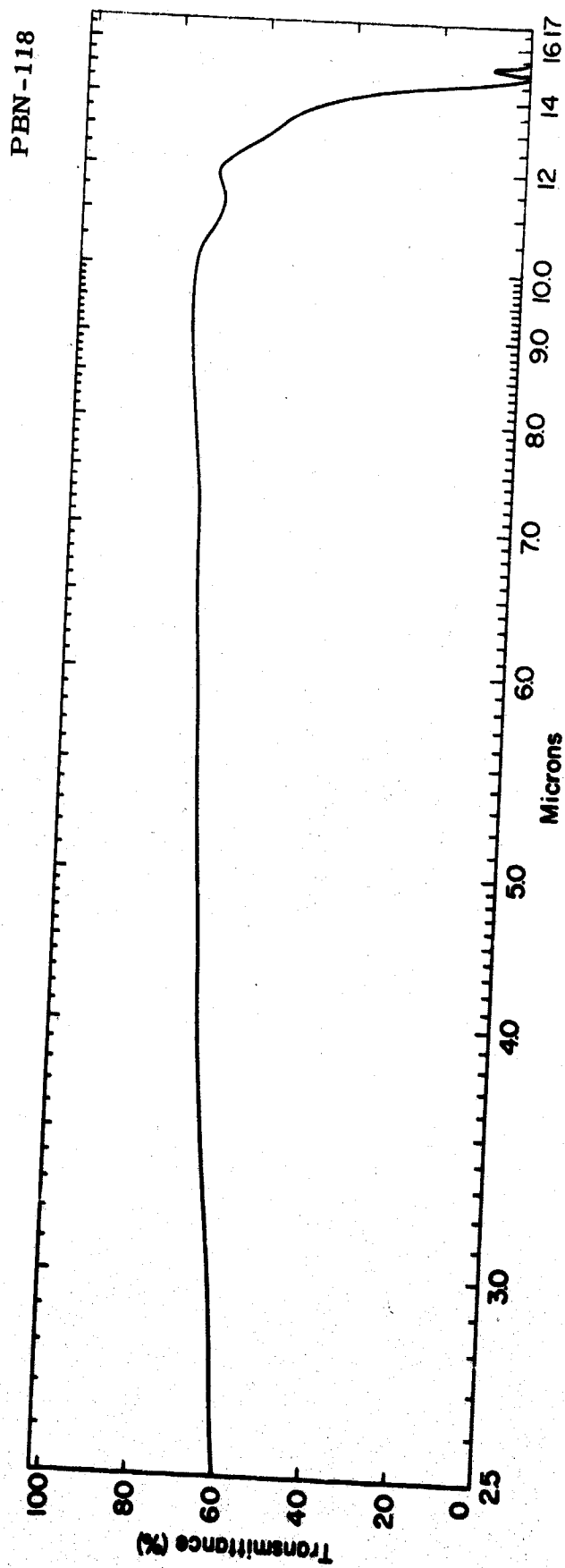


Fig. 2 Infrared Transmission of Run ZS-23.

TABLE V

FLEXURAL STRENGTH TESTS ON CVD ZINC SULFIDE SAMPLES
(From Exploratory Run ZS-23)

Longitudinal Samples

<u>Sample No.</u>	<u>Strength, psi</u>
ZS-23-1	11,110
ZS-23-2	15,210
ZS-23-3	16,000
ZS-23-4	15,080
ZS-23-5	13,270
ZS-23-6	11,010
ZS-23-7	15,580
ZS-23-8	14,960
Avg.	14,230 $\pm$ 2,000

Lateral Samples

ZS-23-9	11,000
ZS-23-10	10,130
ZS-23-11	10,510
ZS-23-12	8,970
ZS-23-13	9,230
ZS-23-14	10,950
ZS-23-15	9,880
ZS-23-16	9,130
Avg.	9,980 $\pm$ 800

SECTION V

SCALE-UP STUDIES - ZINC SULFIDE

One of the goals of this program was to demonstrate the feasibility of fabricating large plates of infrared transmitting material by the CVD process. We proposed to do this by making experimental depositions on 6×12 in. mandrels. Experience has shown that this mandrel is large enough so that most of the problems in making larger sizes would be encountered at this intermediate size. A very good prediction of the feasibility of making $12 \times 24 \times 1/4$ in. plates would be possible from the 6×12 in. depositions.

Usually scaling of CVD processes is best done in steps, solving problems at intermediate sizes before attempting the largest size desired. For this reason two deposition runs (ZS-25 and -26, Table VI) were made on 4×16 in. mandrels before making depositions on larger mandrels.

The first of these runs (ZS-25) yielded a fine-grained material with good in-line infrared transmission. The deposition rate was low and the material was thin, particularly near the exhaust end of the mandrel. This was attributed to the vaporization rate of the zinc. The low deposition rate near the exhaust end of the mandrel resulted from reactant depletion. In this run low-purity (99.9 percent)

TABLE VI

ZINC SULFIDE DEPOSITIONS ON LARGE MANDRELS

Run No.	Pressure (torr)	Gas Flows (lpm)		Reactant in Retort	Reactant Transport Rate (lbs/hr)	Material	Substrate		Temp (°C)
		A	H ₂ S				Size (in.)		
ZS-25	100	15.0	1.5	zinc	.075	PG	4 × 16		690
ZS-26	60	15.0	1.5	zinc	.42	PG	4 × 16		710
ZS-27	60	15.0	1.5	zinc	.50	PG	8 × 16		700
ZS-28	60	11.5	1.5	zinc	.46	PG	8 × 16		680
ZS-29	50	11.5	1.5	zinc	.60	PG	7 × 16		660
ZS-30	50	15.0	1.5	zinc	.20	PG	7 × 16		710
ZS-31	50	15.0	1.5	zinc	.35	PG	7 × 16		710
ZS-32	50	15.0	1.5	zinc	.35	PG	7 × 16		710
ZS-33	40	15.0	1.5	zinc	.75	PG	7 × 16		710
ZS-34	Abort - Ceramic retort failed				---	--	-----		---
ZS-35	40	15.0	1.5	zinc	.43	PG	7 × 16		710
ZS-36	40	15.0	1.5	zinc	0.46	PG	7 × 16		700

zinc was used with no adverse effects on the in-line transmission in the 8 to 14 micrometer band. The material did show a slight yellowish color in the visible which had not been seen when purer (99.999 percent) zinc was used.

A higher zinc retort temperature was used in the next run (ZS-26). The zinc vaporization rate for this run was about six times greater than in run ZS-25, and the deposition rate was also higher. Table VII shows the thickness profile of one plate from this run. The deposition rate was still nonuniform, and much lower at the exhaust end of the mandrel than at the inlet, but was improved compared to the preceding run. The in-line infrared transmission was good. The results of run ZS-26 convinced us that depositions in larger mandrels were feasible. Consequently, we decided to scale up further to 8×16 in. mandrels.

The first run (ZS-27) made on an 8×16 in. mandrel resulted in an extremely low deposition rate, even though the zinc vaporization rate was quite high. These results were attributed to the design of the mandrel, and reactant feed system which resulted in inadequate reactant mixing. The reactants apparently flowed over the mandrel in two more or less separate streams with a minimum of interaction.

TABLE VII

THICKNESS PROFILE (Inches) FOR PLATE A
(Run ZS-32)

Longitudinal Position (in.)	Lateral Position (in.)				
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>
0	0.121	0.165	0.182	0.170	0.165
2	0.132	0.176	0.188	0.182	0.174
4	0.144	0.204	0.209	0.197	0.202
6	0.165	0.230	0.233	0.205	0.223
8	0.173	0.261	0.252	0.242	0.260
10	0.178	0.304	0.278	0.304	0.304
12	0.209	0.355	0.393	0.400	0.210

For the next run (ZS-28) the construction of the mandrel was altered to allow premixing. This run resulted in a considerably higher deposition rate. In some places on the mandrel the material showed excessive internal scatter. The zinc retort was empty at the conclusion of the run, so the zinc vaporization rate could not be determined, but it was obviously much higher than desired.

The next run (ZS-29) was made at a lower retort temperature and a higher furnace pressure. This run resulted in a great deal of "sooting" (deposition of powder) in the mandrel. All of the zinc in the retort was consumed at some point in the run. The "sooting" was attributed to excessive reactant partial pressures, and excessive gas residence times at the mandrel.

For ZS-30 the zinc vaporization rate was reduced by reducing the size of the retort exit aperture, and by drastically reducing the zinc retort temperature. The carrier gas flow was doubled to decrease gas residence times at the mandrel. These measures resulted in a deposition with a uniform flow rate, 1 to 2 mils per hour, over the entire area of the mandrel. There was no sooting. It seemingly confirmed the hypothesis that "sooting" resulted from excessive reactant partial pressure and excessive residence time.

The next run (ZS-31) showed that this hypothesis was incorrect. Considerable "sooting" resulted, although the run was made under conditions similar to ZS-30. A small leak was found in the furnace. This was repaired, and no "sooting" has been experienced since that time.

The next run (ZS-32) was made under deposition conditions similar to those of ZS-31. The vapor inlet and mandrel configuration were slightly altered to smooth out the thickness profile. The furnace was leak-tight and no sooting was observed. The material had a fairly good in-line infrared transmission and a high, but nonuniform deposition rate (Table VIII).

Four longer runs were then attempted with conditions only slightly changed from ZS-32. The goal of these runs was to obtain material large enough to make $2 \times 4 \times 1/4$ prototype samples for validation and shipment to the Air Force.

The first three (ZS-33 to ZS-35) of these runs aborted. The fourth (ZS-36) was successful. The principal problem experienced in making thick runs was inadequate zinc retort capacity. In the interest of speed, improvised retorts were used to obtain a sufficient zinc capacity; in runs ZS-34 and ZS-35 these failed, spilling zinc on the inside of the furnace.

TABLE VIII

THICKNESS PROFILE (Inches) FOR PLATE A
(Run ZS-26)

Longitudinal Position (in.)	Lateral Position (in.)		
	0	2	4
0	0.118	0.122	0.094
2	0.096	0.120	0.090
4	0.073	0.088	0.068
6	0.067	0.083	0.058
8	0.057	0.072	0.049
10	0.041	0.057	0.041
12	0.055	0.052	0.037
14	0.048	0.042	0.033

Run ZS-33 was aborted because a leak developed in the exhaust side of the pump, resulting in unsafe fume discharge into the laboratory.

Run ZS-36 was successful, and two $2 \times 4 \times 1/4$ in. prototype samples obtained from it were polished and shipped to the Air Force. In addition, one $3-1/2 \times 8 \times .225$ in. plate was polished as a demonstration of the feasibility of utilizing the CVD process to make large IR windows. The in-line transmission of this plate is shown in Fig. 3.

The thickness profiles of the raw plates from run ZS-36 are shown in Table IX. The plates are somewhat nonuniform in thickness but this is common in the early stages of the development of a CVD process, and adjustment of the process parameters can usually correct this problem.

Further properties of this run will be found in Sec. VIII.

TABLE IX
THICKNESS PROFILE (Inches) FOR PLATE A
(Run ZS-36)

Longitudinal Position (in.)	Lateral Position (in.)						
	0	1	2	3	4	5	6
0	-----	-----	0.052	-----	-----	0.286	0.198
1	-----	0.241	0.194	0.095	0.118	0.261	0.167
2	0.264	0.336	0.224	0.225	0.169	0.250	0.161
3	0.256	0.348	0.412	0.336	0.187	0.239	0.163
4	0.254	0.359	0.418	0.416	0.206	0.238	0.165
5	0.244	0.366	0.417	0.411	0.224	0.232	0.172
6	0.231	0.354	0.407	0.413	0.240	0.233	0.171
7	0.217	0.346	0.401	0.405	0.263	0.223	0.162
8	0.202	0.332	0.384	0.391	0.271	0.207	0.168
9	0.207	0.331	0.376	0.378	0.257	0.209	0.164
10	0.189	0.310	0.362	0.357	0.269	0.204	0.188
11	0.189	0.307	0.348	0.347	0.265	0.187	0.176
12	0.191	0.296	0.339	0.353	0.253	0.183	0.159
13	0.178	0.273	0.326	0.339	0.268	0.190	0.148
14	-----	0.262	0.322	0.328	0.264	0.185	-----
15	-----	0.250	-----	-----	0.272	-----	-----

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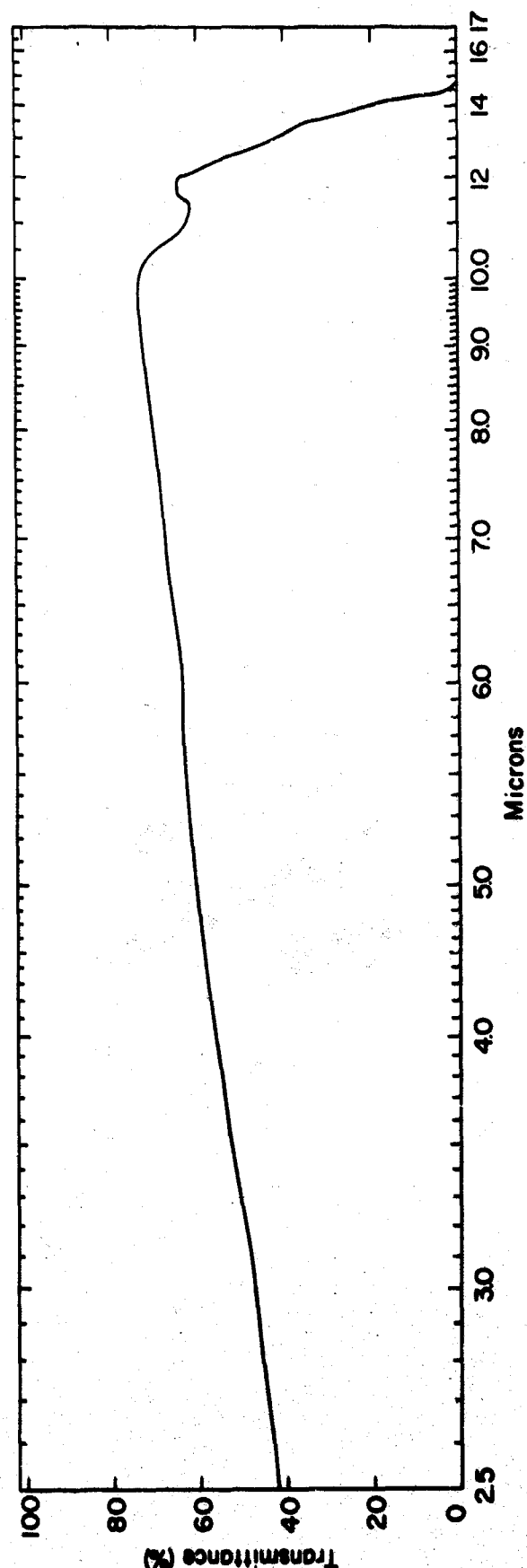


Fig. 3 Infrared Transmission of Run ZS-36.

SECTION VI

CVD CADMIUM SULFIDE

In order to demonstrate the feasibility of using the CVD process to fabricate materials other than zinc sulfide, experiments were conducted with cadmium sulfide. This material was chosen because it could be deposited with minimal modification of the CVD equipment and process used for zinc sulfide. The resulting material should be useful at longer wavelengths.

Cadmium sulfide is softer and weaker than zinc sulfide, but no more so than zinc selenide, another candidate material. Chemical vapor deposition of the latter is much more expensive, both because of the more expensive reactants and because of the precautions required by the toxicity of the materials involved. For these reasons, cadmium sulfide was chosen for exploratory runs.

The first few cadmium sulfide runs were made in the same small two-zone furnace used for the exploratory zinc sulfide runs (see Sec. IV). The deposition conditions initially used were the same as the more successful exploratory zinc sulfide run (ZS-23), except that the retort and mandrel temperatures were lowered by one hundred degrees, based on the relative vapor pressures of zinc and cadmium metals, and their sulfides. This was a good first approximation.

since the first cadmium sulfide run (CS-1 of Table X) turned out well, albeit a little thin.

The next deposition (CS-2) made on a $1\frac{1}{2} \times 8$ in. mandrel yielded material with a higher infrared transmission (Fig. 4), a more uniform thickness profile, and a higher deposition rate than the previous deposition (CS-1). This deposition was made at a higher sulfur-to-cadmium reactant ratio than the first run, and apparently resulted in better infrared properties. No absorptions, other than intrinsic, could be identified from the infrared scans of either run. This is in strong contrast with the experience of other workers who encountered great difficulty in eliminating the 9 micron absorption from hot pressed cadmium sulfide. Also, no black spots could be found in this material, again in contrast with hot pressed material. The infrared transmissivity of this run compared favorably with the transmissivity of state-of-the-art hot pressed cadmium sulfide and chalcogen glasses, particularly when one considers that this was only the second deposition of this material. The low-angle scatter of this run measured at $6328 \text{ \AA}$ was about one milliradian.

Encouraged by this success we attempted to make depositions on 8×16 in. mandrels, in the same set-up successfully used to make large zinc sulfide plates. The same conditions used for ZS-36 were employed for CS-3, except the deposition and retort temperatures

TABLE X

CVD CADMIUM SULFIDE DEPOSITIONS

Run No.	Pressure (torr)	Gas Flows (lpm)		Reactant in Retort	Reactant Transport Rate (lbs/hr)	Substrate		Temp (°C)
		A	H ₂ S			Material	Size (in.)	
CS-1	100	3.0	0.32	cadmium	0.11	PG	1-1/2 × 12	610
CS-2	100	2.3	0.48	cadmium	0.07	PG	1-1/2 × 12	600
CS-3	40	15.0	1.5	cadmium	0.52	PG	7 × 16	600
CS-4	100	11.5	1.5	cadmium	0.75	PG	7 × 16	540
CS-5	100	11.5	1.5	cadmium	0.50	PG	7 × 16	520
CS-6	100	11.5	1.5	cadmium	0.37	PG	7 × 16	520
CS-7	100	11.5	1.5	cadmium	0.68	PG	7 × 16	540
CS-8	80	11.5	1.5	cadmium	0.10	PG	4-1/2 × 15	540
CS-9	80	11.5	1.5	cadmium	0.37	PG	4-1/2 × 15	540

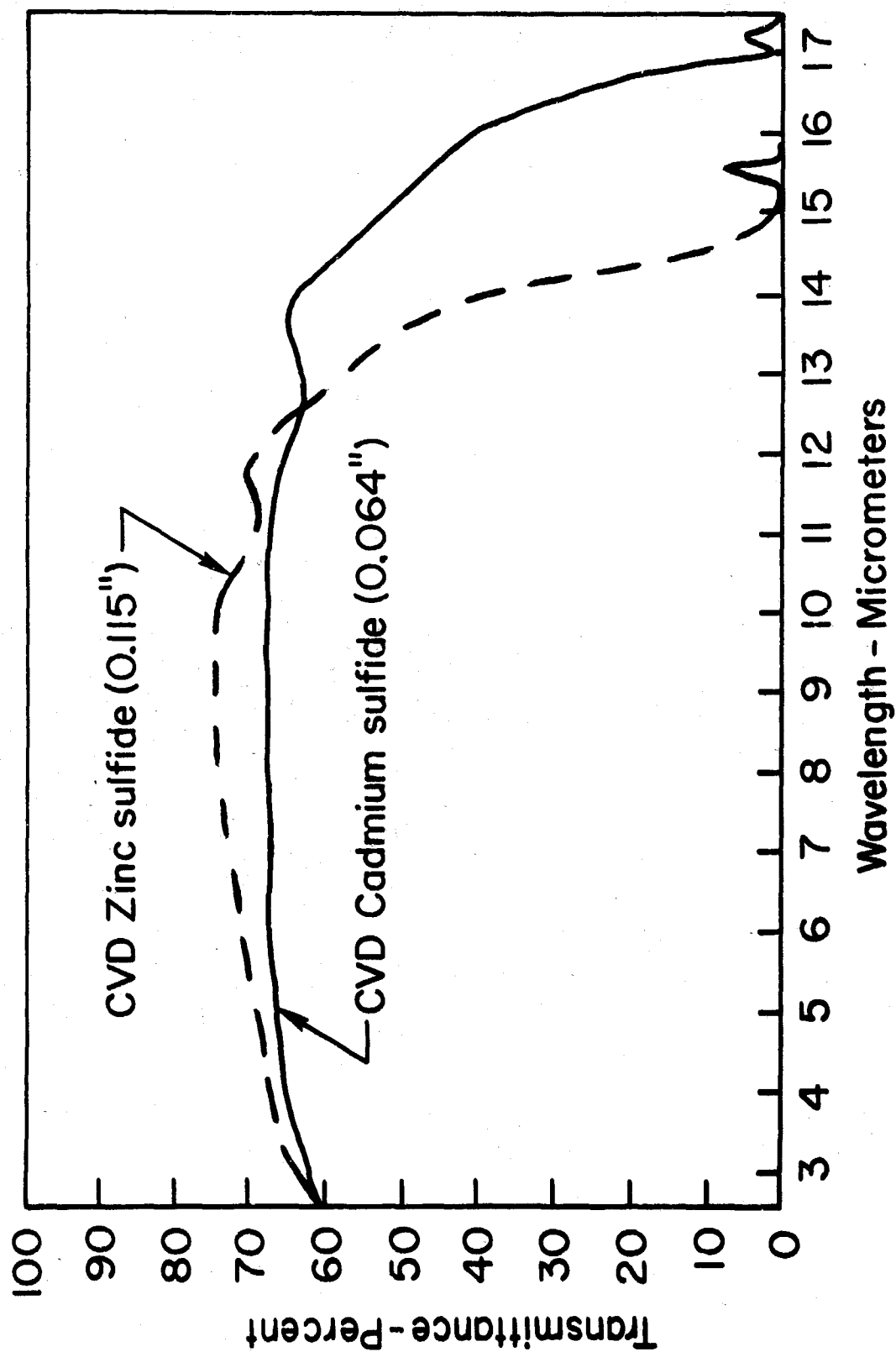


Fig. 4 Infrared Transmission of CVD Zinc Sulfide (ZS-26) and Cadmium Sulfide (CS-2).

were lowered by about 100°C. These temperatures were apparently too high, and the resulting material was much too thin.

The next run, CS-4, failed because of an internal H₂S leak in the furnace which bypassed the mandrel.

The next run, CS-5, was made at a low retort temperature. The material was nonuniform in thickness, being much thicker at the inlet end than the exhaust end of the mandrel. It was also nodular. The nodules apparently caused cracking of the deposition.

The next run CS-6 was also run on 8 × 16 in. mandrels. The retort temperature was about 530°C, and yielded the desired cadmium vaporization rate. Due to the furnace configuration the mandrel temperature could not be properly controlled and was highly non-uniform both spatially and temporally. It ranged from 600° to 700°C. As a result of the high mandrel temperature, the grain size of the deposit was large. Because of this and the nodularity of the deposit, the strength was low, averaging only 2800 psi. A toluene density of 4.811 gms/cm³ was measured on material from this run. A piece 1 × 2 × 0.210 in. was polished and yielded an in-line transmission over 60 percent from 2.5 to 14 micrometers (Fig. 5). The thermal conductivity was 0.033 cal/cm sec °C at room temperature, and the thermal

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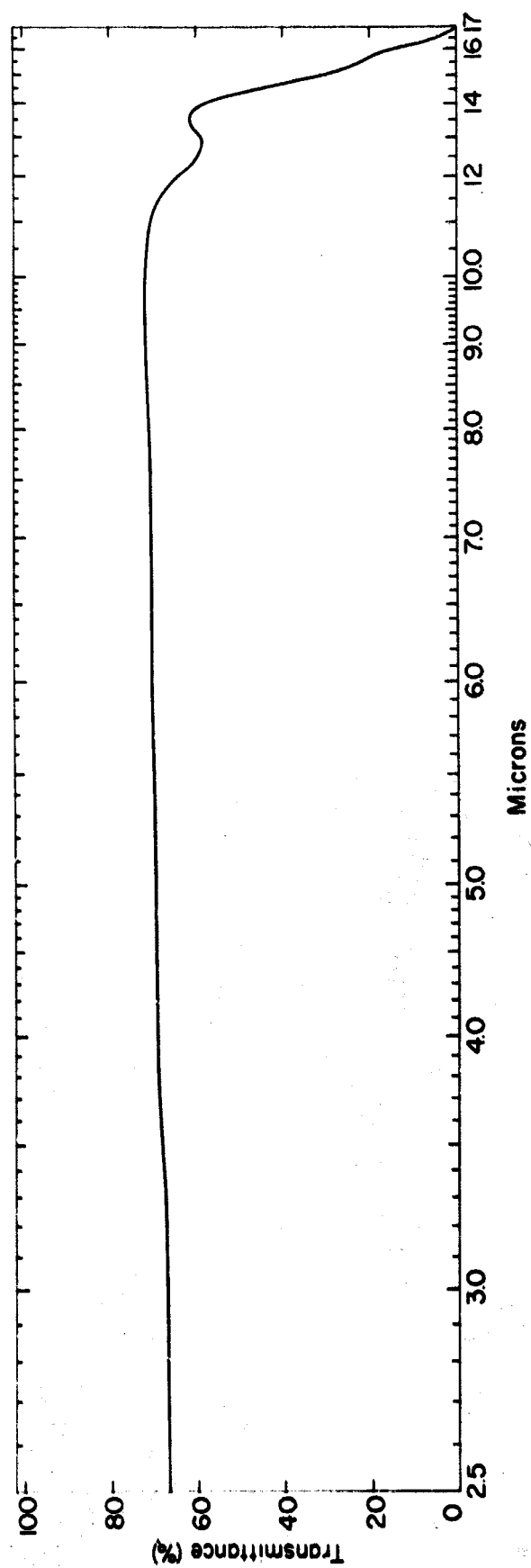


Fig. 5 Infrared Transmission of Run CS-6.

expansion coefficient ranged from 3.6×10^{-6} at 160°C to 5.05×10^{-6} at 450°C .

The next run (CS-7) was the last to be made using the 7×16 in. mandrel. The furnace temperature was controlled so as to hold the cadmium retort temperature between 540° and 560°C . The temperature monitored at the center of the mandrel was 645°C during most of the run. The material resulting from this run was very nodular, and the grain size was much larger than desired. As a result the material was weak, and fractured easily both on the mandrel and in subsequent handling. It was concluded that this was the result of too high a mandrel temperature, excessive cadmium flow, and improper mandrel configuration. A review of runs in smaller mandrels, from which material with good properties was obtained, showed that the mandrel temperature was about 560°C , or about 100°C cooler than this run.

It was decided to make the next run (CS-8) at a mandrel temperature of 560°C . In order to do this without affecting the retort temperature, a special retort heater was constructed and installed in the furnace. This permitted independent control of the mandrel and retort temperatures. At the same time the mandrel configuration was changed to a closed end box, $4\frac{1}{2} \times 4\frac{1}{2}$ in. square by 15 in. long.

This run yielded a fine-grained material with very few nodules. A strength of 7800 psi was measured in flexure. Unfortunately, the cadmium vaporization rate was very low, and as a result the material was very thin (about 0.050 in.). The low vaporization rate was attributed to an improper flow pattern of argon carrier gas through the cadmium retort, and possibly an H_2S leak into the retort.

SECTION VII

MANDREL MATERIALS FOR CVD ZINC AND CADMIUM SULFIDE

The mandrel material selected as a substrate for chemical vapor depositions can mean the difference between success and failure. Ideally, the mandrel material should be chemically inert to the reactant vapors, the waste vapors, and the product. Its thermal expansion coefficient should either be equal to that of the product to avoid introducing undesirable stresses during heatup or cooldown; or it should be either much large for o. d. depositions or much smaller for i. d. depositions. It should be provided with the proper microfinish to seed the desired microstructure in the deposit. Finally, and most importantly, it should either release readily from the deposit if the CVD material is to stand alone, or it should bond firmly and uniformly if it is to remain a structural part of the deposit.

Several mandrel materials were tried as substrates in our exploratory zinc sulfide runs. Fused silica yielded good results provided it was perfectly clean and well polished. Unfortunately if it was used more than once, a slight etching occurred resulting in partial adherence of the deposit. The enormous difference in thermal expansion between the mandrel and the deposits then caused one or both to "craze"; the failure appearing as a network of fine cracks over the entire surface of that piece.

The use of polished or glazed alumina eliminated the "crazing," because the thermal expansions of substrate and deposit were then matched. Unfortunately the deposit adhered strongly to the alumina substrate and was difficult to remove. High expansion graphite behaved similarly to alumina.

Molybdenum sheets gave fair results. Unfortunately there seemed to be some reaction between substrate and product, resulting in a discoloration of the deposit. In addition, thin molybdenum sheets were too flexible to be practical; thick ones are considered to be too expensive.

Pyrolytic graphite yielded the best results and was adopted as the standard substrate material. It is dense, impervious, and apparently non-reactive in this system. Neither zinc nor cadmium sulfide adhered to it, and separation of deposit from mandrel was easy. Pyrolytic graphite mandrels could be used repeatedly. Pyrolytic graphite mandrels are formed by either machining from solid plate stock or by deposition on a graphite base.

SECTION VIII

PROPERTIES

1. IN-LINE TRANSMISSIVITY

The in-line transmissivity of zinc and cadmium sulfide samples were measured using a Perkin-Elmer Infrared Spectrometer Model 457. The instrument was calibrated by running both zero and 100 percent transmission curves just before and just after running the sample. A 1/8 in. thick flat of IRTRAN 2 (ZnS) was used as a standard sample, and was scanned just subsequent to the CVD zinc sulfide scan. Normal slit widths, and medium scan speeds were used. Scans were very reproducible.

Figure 3 shows the in-line transmissivity of a sample of CVD zinc sulfide taken from the same deposition run as the $2 \times 4 \times 1/4$ prototype plates. The sample had been given a plate-glass finish prior to measurement. It displays over 60 percent transmissivity from 6 micrometers to about 12.5 micrometers. The transmissivity falls rapidly above 12.5 micrometers because of the intrinsic absorption of zinc sulfide. The slow decline in transmissivity at the shorter wavelengths is an indication of internal scattering.

The in-line transmissivity of the $2 \times 4 \times 1/4$ prototype CVD ZnS plates measured at 10 micrometers was substantially the same irrespective of location.

Each of the plates was mounted in turn in the sample chamber of a thoroughly stabilized Perkin Elmer Model 457 dual-beam spectrometer. A linear amplifier with a gain of ten was connected to the output of the Perkin Elmer instrument, and this in turn fed a rapid-response recorder. The amplifier was designed so that precise offset voltage could be applied to the signal before it entered the recorder so that, in effect, a recording could be made at ten times the original sensitivity of the spectrometer. One scale division of the auxiliary recorder chart thus represented 0.1% change in the in-line transmissivity of the sample.

The spectrometer was set at 10 microns, at which point the in-line transmissivity for each sample was near theoretical. The offset voltage on the auxiliary amplifier was adjusted to place the auxiliary recorder at mid-scale, with a gain of ten.

Each sample was then slowly traversed over the sampling slit, with the auxiliary recorder running, thus measuring the change in in-line transmission with position on the sample. Several scans were made on each sample, so as to cover the entire area; then a new sample was introduced. The measurements were then repeated with different sampling slit widths.

The results consistently showed a maximum deviation of less than 0.1 percent for in-line transmissivity over the entire area of any

given $2 \times 4 \times 1/4$ in. sample of zinc sulfide, and less than 0.5 percent from sample to sample. The latter can probably be attributed to differences in thickness and polish rather than any real variation in transmission.

A similar measurement was made of the uniformity of in-line transmissivity in the thickness direction. For this measurement the polished faces were cut normal to the deposition plane and parallel to the thickness direction, so that traversing the sample over the sampling slit would measure the change in in-line transmissivity with position in the thickness direction. A very narrow (0.050 in.) sampling slit was used to obtain good spatial resolution. This lowered the signal-to-noise ratio so that any change in transmission which was less than 0.2 percent was masked by system noise. The in-line transmissivity through one-quarter inch of zinc sulfide in general varied less than 1 percent in the thickness direction of the as-deposited sample.

CVD cadmium sulfide displayed excellent in-line transmissivity, with no evidence of any impurity absorption from 2.5 to 14 micrometers. Figure 5 is a scan of a polished piece of run CS-6, 0.210 in. thick, which shows an in-line transmissivity of over 65% from 2.5 to 12 micrometers, and over 60 percent from 2.5 to 14 micrometers. The transmissivity falls off rapidly above 14 micrometers because of the intrinsic absorption of cadmium sulfide. The lower transmissivity

at 12.5 micrometers is apparently intrinsic.⁽³⁾ The internal scattering of cadmium sulfide is very low, as indicated by the high transmissivity at short wavelengths.

2. REFRACTIVE INDEX

The refractive index of solids in the infrared range is normally found by fabricating a prism and measuring the angular deviation of a collimated beam passed through it. At this early stage of our material processing, the scattering of such a beam is too great to allow a precise measurement of beam deviation. Accordingly, we devised an alternate technique to avoid the scatter problem, namely the fabrication of a Fabry-Perot plate, using the Fresnel surface reflections to generate a set of interference fringes in the transmission spectrum of a thin plate. This technique is simple, and worked well, at least outside of the absorption bands. It can also be adapted very simply for measurements at high temperatures. The refractive index was found to be constant to within 1 part in 200 at wavelengths between 2.5 and 11 micrometers. The absolute value is $2.28 \pm .025$, an accuracy limited by thickness measurement. An apparent change of 7 percent occurred at wavelengths between 11 and 16 micrometers, but this may have been influenced by the associated absorption and is still being analyzed.

3. DENSITY

Twelve (12) density samples were cut from various positions of a 6 X 12 X 0.3 in. plate from run ZS-36, as shown in Fig. 6, and their density was measured by the immersion method using toluene as the fluid. The maximum variation from sample to sample was 0.005 gm/cm^3 , as shown in Table XI. Some of the samples were then cut in half to determine if density variations existed through the thickness. The maximum variation in density measured by toluene immersion was 0.004 gm/cm^3 .

The bulk density was measured on a single sample by accurately measuring its dimensions and weight. The result was $4.083 \pm 0.004 \text{ gm/cm}^3$, a value which agreed well with the toluene immersion data.

The toluene immersion densities of two samples of CVD cadmium sulfide run CS-6 were 4.79 and 4.81 gm/cm^3 . The handbook value for the density of cadmium sulfide is 4.82 gm/cm^3 .

4. FLEXURAL STRENGTH

The flexural strength of CVD zinc sulfide and cadmium sulfide was obtained in three-point loading. Several measurements using four-point loading were made as checks on the method.

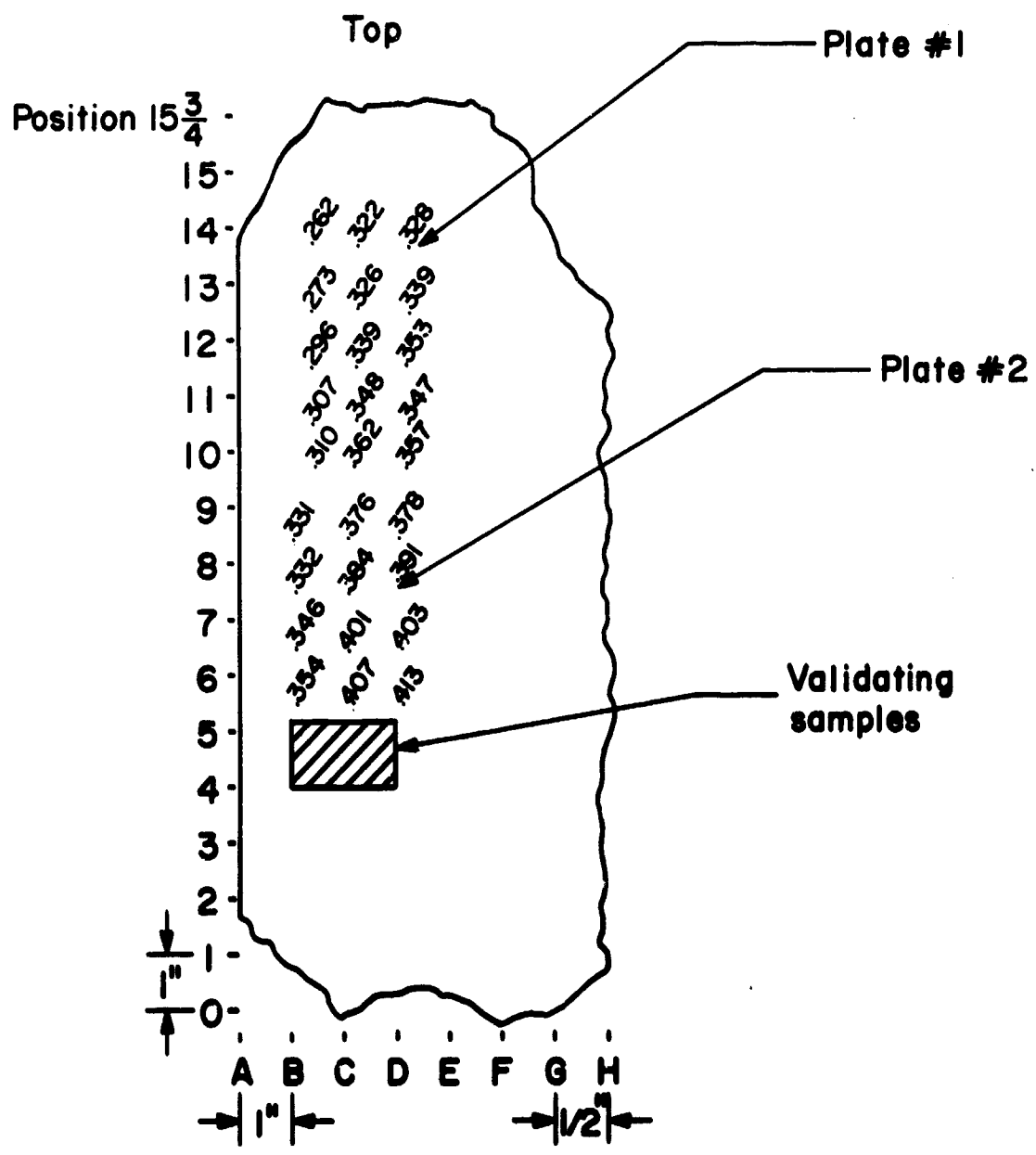


Fig. 6 Location of Samples (ZS-36).

TABLE XI

DENSITY OF CVD ZnS AT VARIOUS POSITIONS
(Run ZS-36)

<u>Position</u> <u>(Fig. 6)</u>		<u>Sample Wt.</u> <u>(grams)</u>	<u>Toluene</u> <u>Immersion Density</u> <u>(grams/cm³)</u>
1B		2.93	4.083
1D		1.61	4.078
1H		1.57	4.086
5A		3.11	4.077
5D		3.43	4.082
5H		1.89	4.082
10B		2.80	4.082
10D		4.13	4.081
10H		3.13	4.082
14B		3.41	4.081
14D		4.57	4.081
14F		1.91	4.083
1B	First deposited	1.09	4.079
1B	Last deposited	1.61	4.075
5D	First deposited	1.59	4.080
5D	Last deposited	1.60	4.077
10D	First deposited	1.78	4.086
10D	Last deposited	2.10	4.081
14D	First deposited	2.15	4.080
14D	Last deposited	2.11	4.079

Thirty-eight (38) specimens of zinc sulfide obtained from run ZS-36 were tested at room temperature. These samples were obtained from various positions on the plate; they were cut longitudinal, transverse (with respect to the 6 X 12 in. direction), and from the substrate and deposition sides of the deposition. No significant differences, regardless of sample position, were observed. The average strength from this run was $11,000 \pm 1300$ psi (Table XII).

The flexural strength of samples from this same run was measured at temperatures up to 500°C (Table XIII). The flexural strength declined slowly with increasing temperature, being about 15 percent lower at 500°C than at room temperature.

The modulus of elasticity was determined from the deflection of the test specimens in the flexural tests, and was 10.8×10^6 psi for run ZS-36.

The flexural strength determined on specimens of run ZS-23 was 14,100 psi (Table V). This sample was deposited at a lower mandrel temperature than run ZS-36 and was consequently finer grained. The difference in grain size probably accounts for the difference in strength.

TABLE XII

MEASURED ROOM TEMPERATURE FLEXURAL STRENGTHS
INDIVIDUAL BEAMS OF CVD ZnS - RUN ZS-36

A. Samples taken parallel to vapor flow (Pos. 4 to 5, G to H) (Fig. 6)

First Deposited		Last Deposited	
Sample No.	Strength (psi)	Sample No.	Strength (psi)
1	10,000	1	11,860
2	9,130	2	9,700
3	8,990	3	10,110
4	10,720	4	11,180
5	11,150	5	11,750
6	13,220	6	12,160
7	11,940		
8	12,110		
Avg. 10,910 $\pm$ 1500		Avg. 11,130 $\pm$ 1000	

B. Samples taken perpendicular to vapor flow (Pos. 4 to 5, G to H) (Fig. 6)

1	11,740	1	9,310
2	11,170	2	8,950
3	10,770	3	9,350
4	10,640	4	9,320
5	10,500	5	11,600
6	12,300	6	11,430
7	13,220	7	12,960
8	14,160	8	10,700
Avg. 11,810 $\pm$ 1325		Avg. 10,450 $\pm$ 1450	

TABLE XII (Cont'd)

C. Samples taken from pos. 7 to 8 (G to H) (Fig. 6)

<u>Sample No.</u>	<u>Strength (psi)</u>
1	10,300
2	11,340
3	11,430
4	11,730
Avg.	11,200 $\pm$ 620

Overall average strength (34 samples) = 11,090 $\pm$ 1310

TABLE XIII
PROPERTIES OF CVD ZINC SULFIDE
(Run ZS-36)

Density (gm/cc)	4.08
Flexural strength (psi) @ RT	11,100 $\pm$ 1300
200°C	10,900
300°C	10,700
350°C	9,400
500°C	9,500
Young's modulus (psi)	10.8×10^6
Poisson's ratio	0.33
Thermal conductivity (RT) watts/cm/°C	0.15
Thermal expansion coefficient ($\times 10^{-6}/^\circ\text{C}$)	
RT to 200°C	6.95
RT to 400°C	7.48
RT to 600°C	8.08
RT to 800°C	8.37
In-line transmissivity @ 6 to 12 microns (1/4 inch thickness)	> 60%

The flexural strength of CVD cadmium sulfide showed a similar but even more extreme dependence on grain size. The room temperature flexural strength of run CS-6, which was run at a high mandrel temperature and consequently was large grained, was only 2800 ± 180 psi, whereas the strength of run CS-8, which was run at a much lower mandrel temperature and consequently was finer grained, was 7800 ± 320 psi.

5. THERMAL LIMIT OF USEFULNESS

The thermal conductivity of CVD ZnS was measured on a polished sample of run ZS-36 at room temperature using a TPRG thermal comparator. The measured value of 0.15 watts/cm/°C agreed very closely with the literature value for commercial hot pressed zinc sulfide of IR window quality. The thermal conductivity of CVD cadmium sulfide run CS-6, measured similarly, was 0.14 watts/cm/°C. This agrees well with the data reported for hot pressed cadmium sulfide of window quality. (4)

The thermal expansion coefficient for zinc sulfide run ZS-36 (Table XIII), and cadmium sulfide run CS-6 (Table XIV) were measured on four samples, using a Leitz dilatometer. The measured values agree well with those in the literature for hot pressed materials of window quality.

TABLE XIV
PROPERTIES OF CVD CADMIUM SULFIDE

Density (g/cm ³) @ RT	4.80
Flexural strength (psi) @ RT	7800
Thermal conductivity (RT) watts/cm/°C	0.14
Thermal expansion coefficient (× 10 ⁻⁶ /°C)	
RT to 200°C	4.35
RT to 400°C	4.94
RT to 500°C	5.24
In-line transmissivity @ 2.5 to 14 microns (0.200 in. thickness)	> 60%

The index of refraction, and the in-line transmissivity of CVD zinc sulfide (ZS-36) was measured at 200°C using a special sample heater attachment to the Perkin Elmer 457 Spectrophotometer. A slight shift of the cutoff wavelength towards shorter wavelengths occurred but there was no other untoward effect.

A polished CVD zinc sulfide sample ZS-36 was heated to 500°C in air for 30 min. Its in-line transmission measured before and after this treatment showed no measurable change.

Polished samples of CVD zinc sulfide were heated to 500°C and repeatedly quenched in air to room temperature with no apparent damage either structurally or optically.

As noted previously, the flexural strength of CVD ZnS did not deteriorate markedly at temperatures as high as 500°C.

On the basis of these data, we conclude that the temperature limit of usefulness for CVD ZnS is above 200°C.

6. X-RAY DIFFRACTION ANALYSIS

X-ray diffraction measurements were made on both CdS and ZnS deposits to assess the presence of cubic vs hexagonal crystal

structure and to see whether the deposits exhibit preferred orientation. In determining the presence of cubic vs hexagonal phase the possibly undesirable effects of preferred orientation were minimized by grinding the deposited material into a fine powder. Diffraction patterns were obtained on a General Electric XRD-5 Diffraction Unit using $\text{CuK}\alpha$ radiation, scintillation detection with pulse height discrimination, and a LiF monochromator between the powder sample and the detector to eliminate scattering from radiation other than $\text{CuK}\alpha$. The diffraction data were collected by point counting, using 0.05° as angular interval and 200 sec as time base. In preferred orientation measurements flat pieces of deposition material were mounted with their deposition-plane normal bisecting the angle between incident and diffracted beam. Diffraction patterns were obtained in the normal acquisition mode, i.e., the diffractometer was driven at constant speed through the angular range of interest and the counting rate was monitored on a strip chart recorder. The nature and degree of preferred orientation was then inferred from the relative intensities of the recorder traces as compared to the relative intensities obtained earlier for powdered samples.

a. CdS Results

A comparison of the cubic vs the hexagonal diffraction pattern of CdS indicates that in the range of the first dozen hexagonal reflections

only the two cubic reflections (200) and (400) are not coincident with hexagonal reflections; the ASTM Powder File lists the cubic (200) and (400) intensities as 40 and 20, respectively, relative to 100 for the strongest cubic line. Our pattern for finely ground CdS showed only hexagonal peaks. The angular range where the cubic (200) and (400) should appear revealed not even a hint of a background variation although comparably strong hexagonal peaks showed an intensity of about 20,000 counts/200 sec above a background of a few hundred counts/200 sec. From this finding we conclude that the CdS deposits are essentially pure hexagonal. They exhibit a strong preferred orientation in which the hexagonal basal plane favors alignment with the deposition plane. This is clearly evident from the strong intensity of the hexagonal (002) and from the absence of the diffraction peaks (100) and (110) in the diffraction trace of flat deposited plates. In randomly oriented material, e. g., the finely ground powder, both the (100) and (110) reflections are stronger than the (002).

b. ZnS Results

A comparison of cubic vs hexagonal ZnS indicates that several purely hexagonal peaks are contained within the range of the first half dozen cubic peaks. The strongest of the hexagonal peaks is the (100), listed in the ASTM Powder File with a relative intensity of 100. Other "clean" hexagonal peaks are the (102) and (103) whose relative intensity

is about 50. Our pattern for finely ground ZnS showed predominantly peaks of the cubic phase. Of the "clean" hexagonal peaks, only the (100) was observed as a weak shoulder of several hundred counts/200 sec next to the strong cubic (111), whose intensity was over 50,000 counts/200 sec. The positions of the hexagonal (102) and (103) showed no clear background variation. This suggests that the small amount of hexagonal phase that is present has some preferred orientation favoring the (100). The total content of hexagonal phase is estimated to be of the order of one percent or less. Since the bulk of the deposits is cubic their preferred orientation, if any, was not investigated.

SECTION IX

CONCLUSIONS

The feasibility of utilizing the chemical vapor deposition process for forming infrared windows was demonstrated by making $2 \times 4 \times 1/4$ plates of CVD ZnS whose properties were comparable to those of hot pressed ZnS of optical quality. The feasibility of scaling the process to make large infrared windows was demonstrated by making $6 \times 12 \times 1/8$ in. plates of CVD ZnS.

The process can be modified to fabricate materials other than zinc sulfide. Cadmium sulfide was deposited on 6 12 in. mandrels, although some difficulties with nodules were experienced. It is probable that these can be eliminated by proper modification of the deposition parameters. The optical properties of CVD cadmium sulfide were excellent, with a low-angle scatter of about 1 milliradian in the visible, and an in-line transmissivity greater than 60% from 2.5 to 14 micrometers for a thickness of 0.200 in.

Pyrolytic graphite yielded the best results of the various materials tried for substrates, and was adopted as the standard mandrel material. It is dense, impervious, and apparently non-reactive with the sulfides. Neither zinc nor cadmium sulfide adhered to it and separation of the deposit from the mandrel was easy. Pyrolytic graphite mandrels could be used repeatedly.

Conventional CVD was better suited to the fabrication of infrared materials than was transport CVD. The latter yielded poor results, both in terms of grain size and in the incorporation of harmful impurities.

The problems encountered in CVD are very different from those which are important in hot pressing or glass casting. Impurity absorptions which cause so much difficulty in the latter two processes were of second-order importance in the same materials made by CVD. Impurity absorptions were rarely seen in infrared scans of CVD zinc and cadmium sulfide material made by conventional CVD in a dynamic system. This is apparently the consequence of the distillation processes which automatically accompany the generation of the reactive vapors. On the other hand, nodule formation was a problem peculiar to CVD, and much effort had to be devoted to eliminating it. Another problem which has not been completely overcome is optical scatter in CVD zinc sulfide. The small-angle optical scatter in CVD cadmium sulfide was much less than for CVD zinc sulfide.

The important properties of CVD zinc sulfide material taken from a single run were substantially the same irrespective of location on the plate. The in-line transmissivity measured at 10 micrometers varied less than one-half of one percent from the mean regardless of the sampling position. No significant correlation could be found between sample position and flexural strength.

Property measurements on CVD zinc sulfide at elevated temperatures revealed no significant deterioration at 200°C. Hence, the material should be useful to above 200°C.

SECTION X

RECOMMENDATIONS

The CVD process is not inherently size limited and has the potential for making very large IR windows. This potential should be exploited. The feasibility of making moderate size windows of CVD zinc sulfide and cadmium sulfide has been demonstrated. The process should be further developed so as to make large (12 × 24 in.) plates of one or both of these materials.

Zinc sulfide possesses a considerable advantage over cadmium sulfide in mechanical properties. In addition it is cheaper to manufacture. Its major drawback is that it is useful only out to about 13 micrometers, but for systems operating below this wavelength it is superior. For these reasons, CVD zinc sulfide should be chosen as the initial material to be developed

Before proceeding to the development of 12 × 24 in. plates of zinc sulfide, further experimentation should be conducted in small size mandrels. The purpose of these experiments should be:

- 1) Determine the purity of reactants necessary to achieve the required optical properties most economically.

2) Optimize the deposition parameters so as to minimize crystallite size, internal scattering, and to maximize mechanical strength and optical transmissivity.

3) Obtain data for scaling the process to larger size plates.

Once the properties are optimized, in small size mandrels, development of the process for depositing 12 × 24 in. plates should be initiated.

Later, the CVD process should be developed to fabricate other materials and more complex shapes.

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