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OF PBSSE(U) BARNES ENGINEERING CO STAMFORD CT
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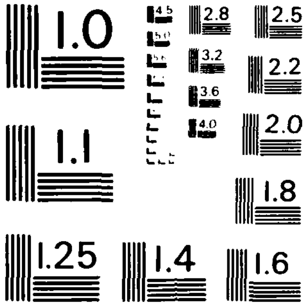

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AD A134 310

FABRICATION OF SCHOTTKY BARRIER DETECTORS ON THIN FILMS OF PbSSe

FINAL REPORT - PHASE I

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FABRICATION OF SCHOTTKY BARRIER DETECTORS ON THIN FILMS OF PbSSe

FINAL REPORT - Phase I

January 1982 - September 1982

Contract #N60921-82-C-0035

BEC Project FEEA

Prepared for

NAVAL SURFACE WEAPONS CENTER
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Silver Spring, MD 20910

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO. [illegible]	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Fabrication of Schottky Barrier Detectors on Thin Films of PbSSe		5. TYPE OF REPORT & PERIOD COVERED Final Technical Report Phase I Jan 1982-Sept 1982
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) W. Rolls		8. CONTRACT OR GRANT NUMBER(s) N60921-82-C-0035
9. PERFORMING ORGANIZATION NAME AND ADDRESS Barnes Engineering Company Government Systems Division 30 Commerce Rd., P.O. Box 53, Stamford, CT 06904		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 62762N;XF62587;004;1R45BD
11. CONTROLLING OFFICE NAME AND ADDRESS Naval Surface Weapons Center White Oak Laboratory, Code R45 Silver Spring, Maryland 20910		12. REPORT DATE December 1982
		13. NUMBER OF PAGES 21
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release: distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Infrared; Detectors

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Thin layers of lead chalcogenide were grown on single crystal BaF_2 substrates using a modified hot wall system. These films were characterized using Hall measurements to determine mobility and carrier concentration. Schottky Barrier diodes were formed using evaporated lead contacts deposited on surfaces which had been activated by a $PbCl_2$ treatment. Evaporated gold was used as the Ohmic contact. Detectors were made by mounting the BaF_2 on copper holders. Interconnections were made using platimum wires and silver epoxy.

PbS, PbSSe, and PbSe films were grown with carrier concentrations in the mid $10^{17}/cm^3$ range at 77°K. Spectral response measurements verified that binary species evaporation was taking place and that use of a secondary source of sulphur or selenium did not result in films of different composition than the primary source. At 77°K, peak D* (500,900,1) values in the range of 6.4×10^9 to 1.4×10^{10} cm $Hz^{1/2}/W$ were obtained. At 300°K, D* is about 2 orders of magnitude lower. This is believed to be due to relatively high carrier concentrations resulting from inadequate temperature control of the secondary chalcogenide source.

Additional discussion of the results and proposed changes to increase the sensitivity of these detectors at both 77°K and room temperature is included.

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Introduction

Thin layers of lead chalcogenides have been grown on single crystal barium fluoride substrates using a modified hot wall system. Experience gained by other workers[1,2] using this type of system has been useful in determining the parameters used to grow low carrier density films in our system. However, since the systems are not identical, some differences in film properties have been noted and will be discussed in the body of the report. Films have been grown and characterized using Hall measurements to determine the mobility and carrier density. The films, as grown, are activated by exposing the surface to lead chloride which is necessary to obtain good Schottky Barrier devices. Lead contacts have been evaporated onto the surface of the layers to form the Schottky Barriers and also gold contacts to form the ohmic contacts. Subsequently the contacts are connected to platinum wires using silver epoxy. After mounting onto a copper holder such that the radiation is incident on the barium fluoride surface, the devices are characterized electrically and optically.

We have found that most devices are fairly sensitive at 77K but relatively insensitive at 300K. This is due to relatively high values of carrier density due to poor control over the secondary chalcogenide source. Discussion of the results and the proposed changes to improve the detectors' sensitivity at both room temperature and liquid nitrogen temperatures are presented.

Source Preparation

Quartz ampoules were fabricated, etched with 3:1 HNO_3/HF solution and rinsed with deionized water. After flaming the ampoules in air with the oxy-hydrogen torch, the ampoules were allowed to cool and loaded with the appropriate amounts of lead and chalcogenide. The ampoules were pumped to less than 10^{-6} torr using an ion pump, backfilled with 400 torr of hydrogen gas and sealed off.

Reaction of the elements was carried out by inserting one end of the ampoule into a high temperature furnace (1000-1200°C depending on the mixture) and keeping the other end cold to prevent high pressure build up. The entire ampoule was then placed in the furnace and rocked to ensure good mixing before being quenched in a water bath. Post annealing was accomplished by heating the ampoule overnight in a furnace held at 800-900°C.

Layer Growth

The basic equipment consists of a vacuum evaporator with a 6" oil diffusion pump, liquid nitrogen cold trap and 18" diameter bell jar with the modified hot wall evaporation system shown in Fig. 1. Most of the evaporations have been carried out with the opening in the "hot wall" tube approximately 2" from the substrate. Freshly cleaved substrates of BaF_2 were loaded into the substrate holder (initially we used a single substrate). Crushed source material was loaded into the source holder and in some cases Se or S was loaded into the secondary source tube. Table 1. Evaporation runs took from 1-3 hrs depending on the source and substrate temperatures. Layers were typically 1-4 μm thick and were type tested using a thermoelectric probe immediately after removal from the chamber. Typically the layers had a number of cleavage steps arising from the BaF_2 substrate. The appearence of the layers was variable, from cloudy to reflective depending on whether a secondary source of either Se or S was incorporated. Early samples were cloudy and tended to be n-type when a secondary source was not included. However, the p-type samples did produce good detectors at 77K although not at 300K.

Some of the problems associated with layer growth such as the attack on Cu electrodes by the overpressure of Se or S, were not experienced in our system.[2] We feel that the setup is not entirely described as being a hot-wall technique but closer to that of an evaporation. Recent work incorporates 2 substrates, one of which has a Hall sample mask to provide electrical measurements of all layers as a matter of course. We have also modified the system shown in Fig. 1 by heat-sinking the secondary source tube when S is used, to reduce the vapor pressure to a level consistent with producing p-type films with a carrier density of 1-3 X 10^{17} cm^{-3}.

Layer Activation

Previous experience has shown detector performance is strongly influenced by the surface of the PbSSe layer prior to deposition of the Schottky Barrier contact, in this case Pb.[2] The presence of both chlorine and oxygen improves the detector performance substantially. Layer activation is carried out by suspending the layer face down over a source of $PbCl_2$ for 24 hrs in an oven held at 200°C. Both the chlorine from the $PbCl_2$ source and atmospheric oxygen are required. The layer/source separation is approximately 0.5 cm.

Hall Measurements

On several layers the measurement of carrier density and mobility was performed using standard 6 contact, Hall bars. The layers were processed photolithographically and etched to produce the required configuration. Gold contacts were evaporated onto the sample using a photoresist lift-off technique. Silver epoxy (E and C 56C) was used to attach leads to the gold electrodes and the sample was mounted on a holder. Measurements were carried out at both 300K and 77K using a 3000 gauss permanent magnet to provide the magnetic field. Each measurement was performed twice to ensure no change of properties had occurred in the film such as cracking of the substrate.

Contact Studies

The deposition of both the Pb and An contacts are themselves not straight-forward. Slow deposition results in a porous dull lead layer and the formation of a non-ohmic gold layer. Initial results with the gold contacts showed that they were non-ohmic. At this point we did not know if the problem was related to the thickness of the gold layer or to the silver epoxy. The gold source was a considerable distance from the device which resulted in a thin film (~100Å) deposited at a low temperature on the semiconductor layer. A number of gold contact pads were evaporated onto both activated and unactivated layers and silver epoxy contacts made to platinum lead out wires. The results are shown in Table 2.

Heat Treatment

Reports by IT&T and NSWC personnel indicate that the device characteristics may be improved by a thermal cycle to ~250°C. The amount of time reported varies considerably but the temperature range is close. Several layers have been tested and then exposed to 250°C for 5-10 min using an infrared heat lamp. Only in the case of a PbS layer did we see any overall improvement. In some cases there was a slight improvement in the 300K detector characteristics, but the 77K sensitivity decreased. In almost all cases both the lead and gold contacts were already evaporated and the silver epoxy contacts in place. Layer #43/36 was tested before heat treatment with only the Pb contacts in place and showed a degradation of impedance afterwards. Layer #55 (PbS) was not tested before heat treatment but after being heated to 240°C for 30 minutes showed good values of D^*_{500} at both 77K and 195K. Table 3.

Contact Evaporation

Both the lead and gold contacts are deposited at a rate of 10-20 Å/sec to form up to 0.5 μm thick pads. The lead contacts are shiny and clean and do not have a porous look to them. Problems of instability have been noted by IT&T[2] when porous lead contacts were encountered. In both cases the source/substrate distance is ~8". We feel that the gold source should be somewhat closer to the substrate than 8" in order to produce a slight diffusion of Au into the layer to form a good ohmic contact.

Detector Characterization

All of the detectors fabricated were electrically and optically tested. Responsivity and D* measurements were performed using a 500K black body and suitable electronics to match the detector impedance. Capacitance was measured on a Boonton 74D Bridge.

The spectral responses of the detectors showed good correlation with the expected curves for PbS, $PbS_{.5}Se_{.5}$ and PbSe as measured at 77K and 195K. This verifies that binary species evaporation was indeed taking place and that the subsidiary source of S or Se was not changing the layer composition from that of the source.[2].

The detectors were mounted face down on a copper fixture using Dow Corning #3110 rubber. To prevent cracking, the substrate was affixed to the copper mount by only 2 of the 4 corners. Leads were brought out through the spaces between the raised corners of the fixture. A repumpable metal dewar was employed to perform the low temperature measurements, usually with a sapphire or zinc sulphide window. The detector response was measured at 300K using a source with a flux of 12.65×10^{-6} watt cm^{-2} and at lower temperatures with a flux of 2×10^{-6} watt cm^{-2}. Where signal levels were sufficiently high the detectors were checked using both sources. D* measurements were carried out with a number of noise matching transformers and the highest value of S/N was used to calculate D*. Responsivity was measured with the 500K source and a known gain in the following amplifier. When measuring responsivity the device impedance can be measured by putting a resistance in parallel with the detector. When the signal value drops to 50%, the detector impedance is equal to the parallel resistance. Using these values of responsivity and impedance the quantum efficiency of the detectors can be computed, once the spectral response has been measured. At this time no attempts have been made to measure the detector impedance as a function of temperature or to plot the capacitance values at a function of bias. Contact impedances have been fairly high ($>100\Omega$) due to the non-concentric nature of the contact pads with the detector and resulting sheet resistance.

Capacitance and "impedance" were measured on a Boonton Capacitance 74D Bridge using as low a signal as possible to avoid averaging the diode dynamic impedance. As can be seen from Table 3, the impedance values are generally lower than those measured using the responsivity measurement. The open circuit voltage and short circuit current were measured with a Keithley 153 microvolt ammeter.

CHARACTERISTICS OF DELIVERABLE DETECTORS
@ 77 K

Characteristic	Layer #43/46	17/32	40	47/49	46/50/51	55
R_0 Ω	---	3k	---	10k	4.5	28k
S μV	96	48	115	195	115	165
N μV	.18	.11	.28	.23	.4	.2
D*(500,900,1)	1.2×10^{10}	10^{10}	10^{10}	2×10^{10}	6.4×10^{9}	1.4×10^{10}
Voc mV	30	9	48	58	55	94
I_{sc} μA	21	25	24	27	17	0.6
* R_0 Ω	2.3k	2k	2.2k	1.3k	< 1k	2k
C pF	4196	4230	3580	4240	2130	3010
V_{ov} μV	9	4.8	--	42	17	42
Area cm²	3×10^{-3}	3×10^{-3}	3×10^{-3}	3×10^{-3}	3×10^{-3}	5.0×10^{-3}
W μwatt cm^{-2}	2	2	2	2	2	2
Active Material	PbSe	PbSSe	PbSe	PbSe	PbSe	PbS

* Values from Booton Capacitance Bridge

Table 3.

References

1. Preparation of Epitaxial Thin Film Lead Salt.
   Infrared Detectors T. K. Chu, A. C. Bouley, G. M. Black
   Proc. S.P.I.E. Washington, April, 1981

2. Single Crystal Alloy Film Infrared Detectors.
   Final Report from ITT to NSWC 1980-1981

* Se Source
+ S Source

EVAPORATION							HALL MEASUREMENTS						DETECTOR CHARACTERISTICS							
							300°K			77°K					77°K			100°K		
	Layer	T_s	T_{sub}	µm	Time (min)	Type	ρ Ω cm	µ	$\begin{bmatrix} n \\ p \end{bmatrix}$	ρ Ω cm	µ	$\begin{bmatrix} n \\ p \end{bmatrix}$	Area, x 10 cm^2	C pF	R v/w	D* 500K	C pF	R v/w	D* 500K	
9	PbSSe	601	408	1.36	30	p	2.7×10^{-2}	371	6.2×10^{17}	2.3×10^{-3}	4.9×10^{3}	5.5×10^{17}	30	21,000		10^{10}	-	-	-	Made detectors
11	PbSSe	577	412	2.45	30	p	3.6×10^{-2}	255	6.8×10^{17}	3.1×10^{-3}	4×10^{3}	5×10^{17}	30	21,000		2.8×10^{9}	-	-	-	Dets
12	PbSSe	590	414	3.75	30	n														2nd Layer
13	PbSSe	565	399	1.85	30	p														
14	PbSSe	585	399	1.5	30	n														2nd Layer
15	PbSSe	597	396	1.9	30	p														
16	PbSSe	597	400	2.3	30	p														2nd Layer
17	PbSSe	596	394	2.35	30	n							3	4,230	800	10^{10}				2nd Layer
18	PbSe	595	400	2.65	30	n	1.2×10^{-2}	512	10^{18}	4.75×10^{-4}	1.8×10^{4}	7.2×10^{17}								
19	PbSe	603	393	3.75	30	n														
20	PbSe	603	401	4.0	30	p							30			2×10^{9}	-	-	3×10^{7}	Dets
21	PbSe	599	402	3.0	30	p							30			1×10^{9}				Dets
22	PbSe	595	396	1.6	30	p														
23	PbSe	600	395	n/m	30	n														
25	PbSe*	545	350	1.6	120	p														
26	PbSe*	548	346	2.1	180	p														Dets
27	PbSe* On #14	556	353	n/m	180	p														Dets
28	PbSe*	542	346	2.45	180	p	2×10^{-2}	510	6×10^{17}	9×10^{-6}	1.7×10^{6}	4×10^{17}								Dets
29	PbSe* On #12	550	345	n/m	180	p							30		-	8×10^{9}	-	-	-	Dets
30	PbSe* On #13	555	352	n/m	180	p														
31	PbSe* On #16	548	352	n/m	180	p														Dets
32	PbSe* On #17	556	353	n/m	180	p														
33	PbSSe	600	403	2.5	30	p														
34	PbSSe	596	402	2.3	30	n														NSWC
35	PbSSe	600	397	2.4	30	n														
36	PbSSe	606	418	3.0	30	r														
37	PbSSe	604	397	2.0	30	p														NSWC
38	PbSe*	552	347	3.6	180	p	3×10^{-2}	500	4×10^{17}	6×10^{-4}	4.2×10^{4}	2.4×10^{17}								Dets
39	PbSe*	550	350	2.9	180	p														NSWC
40	PbSe*	550	345	3.25	180	p							3	3580	-	10^{10}			6×10^{7}	Dets
41	PbSe*	552	356	3.25	180	p														
42	PbSe*	556	345	3.3	180	p														
43	PbSe* On #36	552	354	n/m	180	p							3	4196	1500	1.2×10^{10}			1.6×10^{7}	
44	PbSSe+	550	400	2.5	180															
45	PbSSe+	550	400	2.8	180	n														
46	PbSSe+	550	350	2.0	180	n														
47	PbSSe+	600	400	5.0	75	n														
48	PbSe* On #45	550	350	5.0	180	f														
49	PbSe* On #47	550	350	4.2	180	p							3	4240	7000	2×10^{10}			1.6×10^{7}	
50	PbSSe* On #46	550	350	2.6	180	p														
51	PbSe* On #46/50	550	350	2.3	190	p							3	2130	2800	6.4×10^{9}				
52	PbSSe*	550	350	n/m	180	p														
53	PbSe *	550	350	n/m	170	p														
55	PbS +	525	375	1.6	60	p							5	3010	4200	1.4×10^{10}				

Table I

Layer	Contact	Initial		After 250°C for 5 min	
		R @ 300K	R @ 77K	R @ 300K	R @ 77K
#24	Au	50	9		
#24	Cr/Au	110	30		
Au	Ag Epoxy	5	1.7		
Pb	Ag Epoxy	2.6	0.7		
#24 A	Au	95	Non Ωic Assymmetric	95	30

Table 2

MODIFIED HOT-WALL EVAPORATION SYSTEM

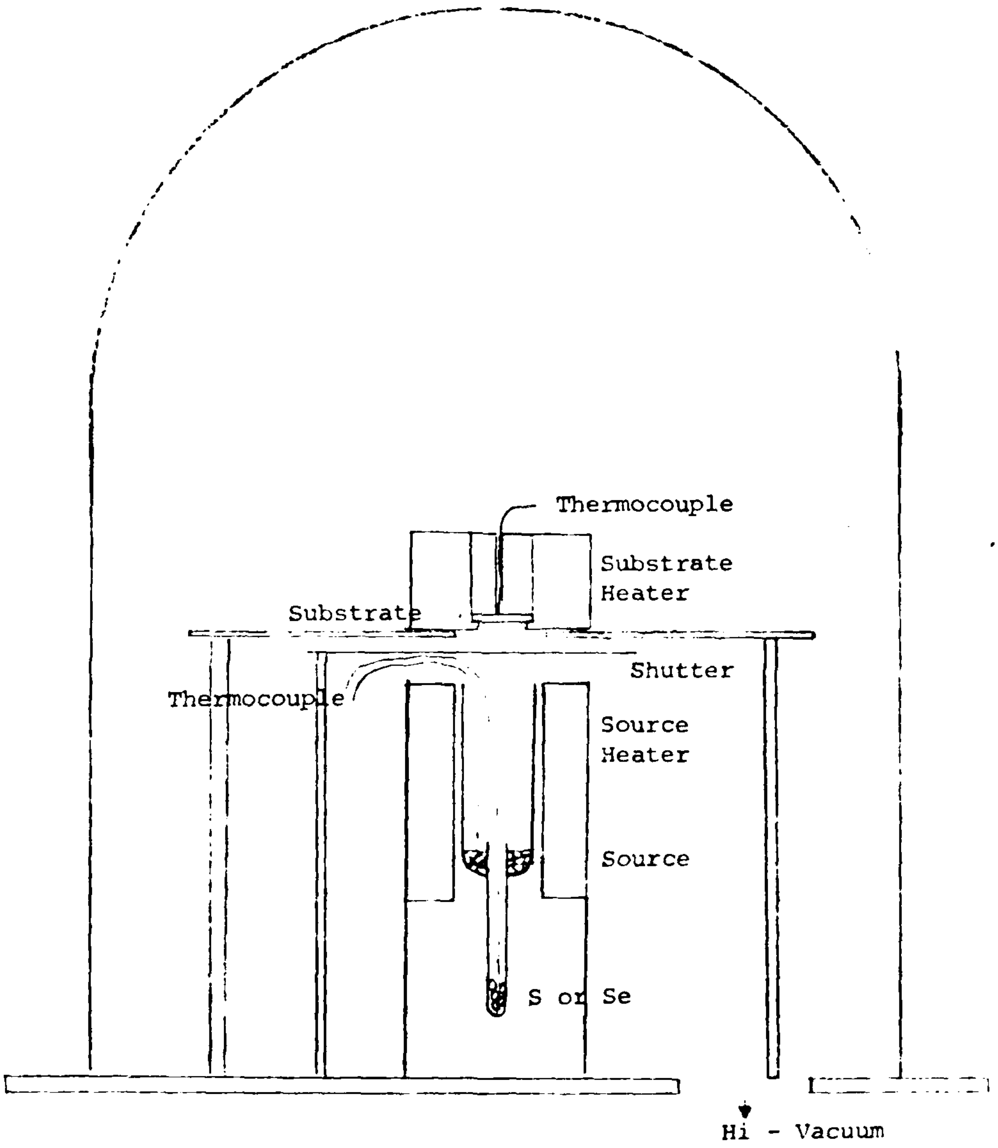
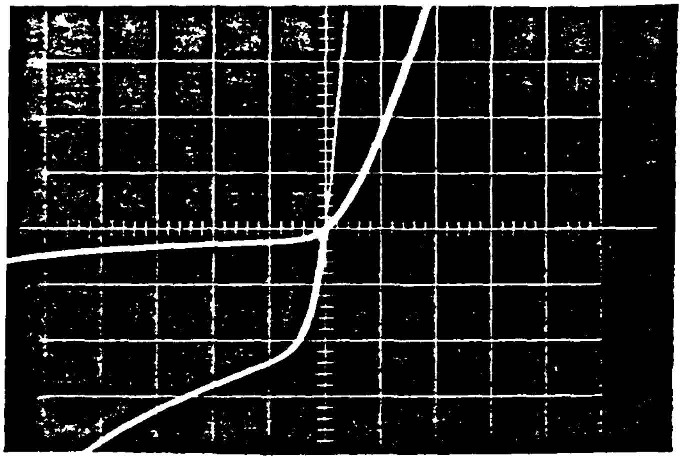


Figure 1

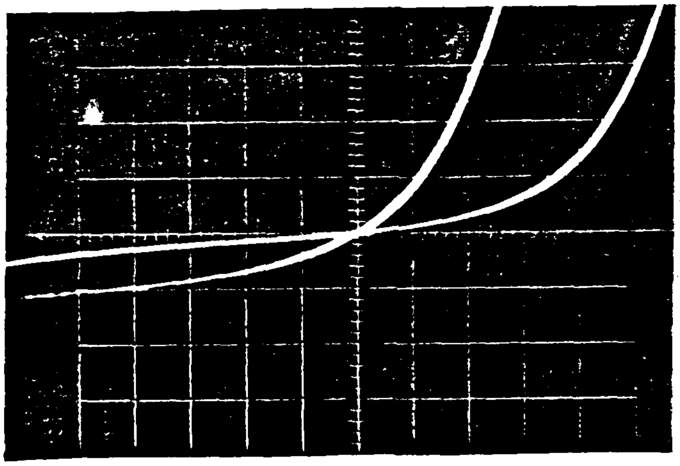
Figure 2



100m V/div
1m A; 0.1m A/div

#47/49

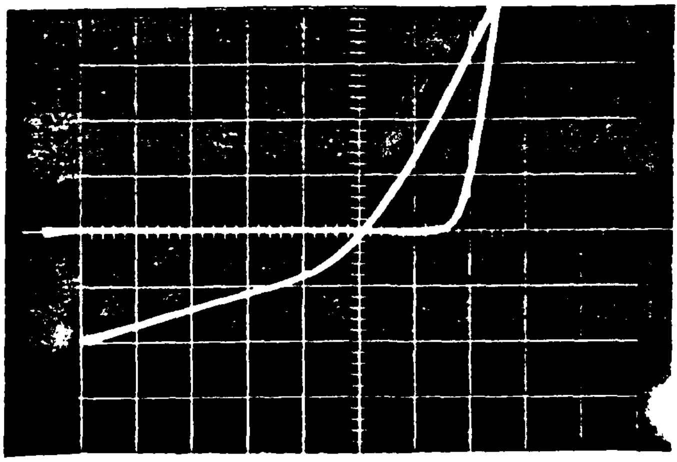
Figure 3



10m V/div
10 µA/div

#47/49 vs Background

Figure 4



100m V/div
100 µA/div

#55 @ 195K and 77K

DETECTOR SPECTRAL RESPONSE

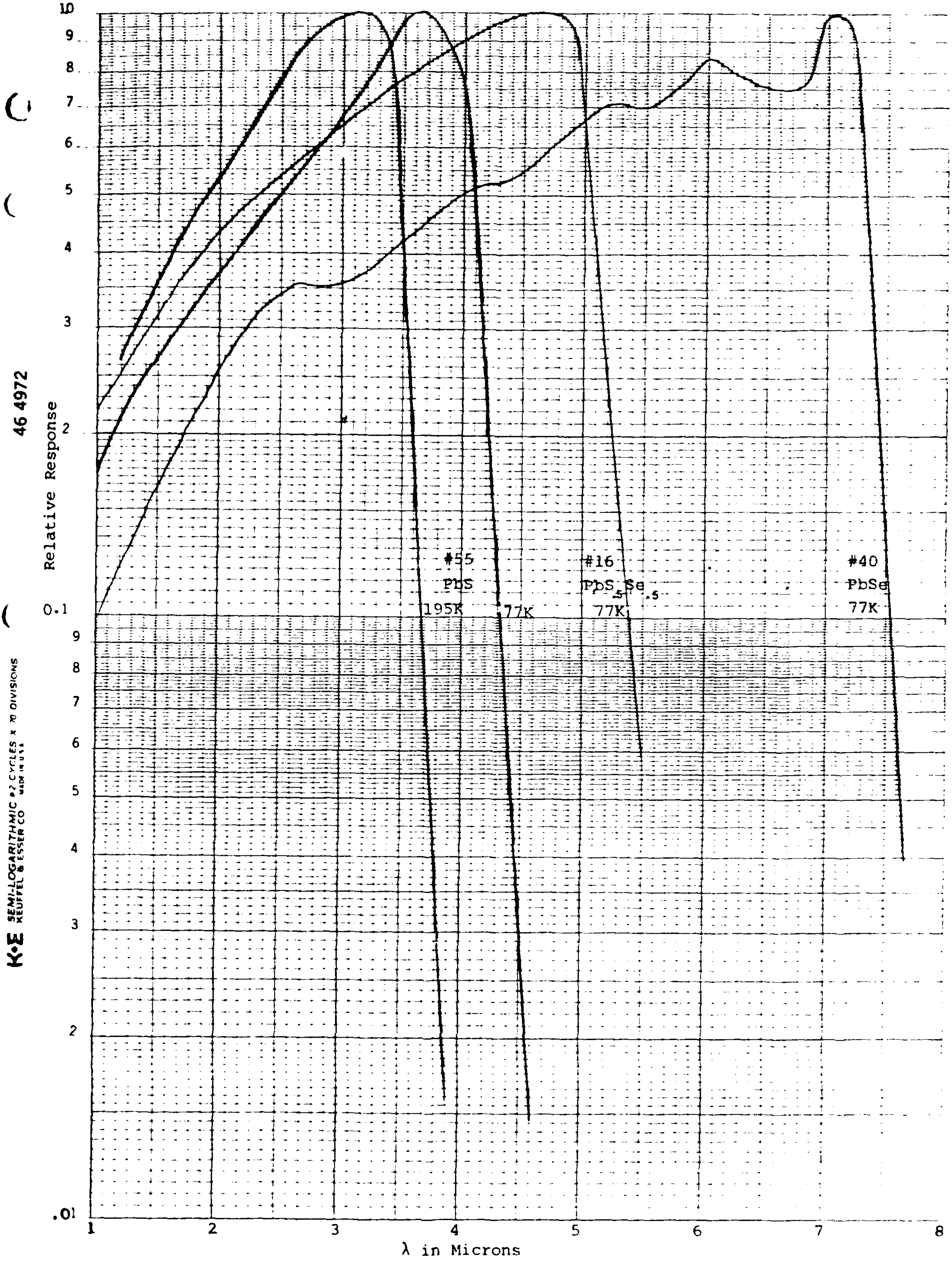


Figure 5

DAT

FILM