varian/611 hansen way/palo alto/california 94303/u.s.a./415/326-4000

ARPA Order No. 306

Program Code No. 421

Contract No. N00014-71-C-0073

Investigator: R. L. Bell
Varian Associates
(415) 326-4000, Ext. 2906

Contractor:
Varian Associates
611 Hansen Way
Palo Alto, California 94303

Scientific Officer:
Director, Physics Division
ONR, 800 N. Quincy Street
Arlington, Virginia 22217

Effective Date of Contract: 15 August 1970

Contract Expiration Date: 14 August 1971

Amount of Contract: $61,098

FINAL TECHNICAL REPORT

"Photoemissive Detector"

Sponsored by

Advanced Research Projects Agency
ARPA Order No. 306

* * *

This research was supported by the Advanced Research Projects Agency of the Department of Defense and was monitored by ONR under Contract No. N00014-71-C-0073.

28

SUMMARY

A program of fabrication of four image tubes using InAsP transmission photocathodes sensitive to 0.965 micron radiation is described. These tubes were intended for imaging parametric upconversion experiments. A number of anticipated difficulties were encountered, and the sensitivity of the tubes shipped was a factor of only ten higher than commercially available image tubes, rather than the factor of 100 believed to be available under the most favorable conditions. The background noise was high, indicating the need for further improvements in tube and process design.

INTRODUCTION

This program was initiated to provide a high-quantum-efficiency imaging detector for parametric up-conversion experiments.[1,2] When the 1.06 micron laser line of Nd^{3+} is used as a local oscillator, for example in proustite, the 10.6 micron line of CO_2 or broad bands of adjacent radiation can be upconverted to the region of 0.965 micron. The occurrence of unexpectedly low power handling capability in proustite had made it a matter of urgency to seek higher sensitivity in the image tube than was available with conventional cathodes at 0.965 micron, and the experimental demonstration in a demountable system by Varian of front surface quantum efficiency of about 12% in this wavelength region with InAsP alloys--a factor of about 100 better than available from conventional photocathodes--(see Fig. 1) suggested the development of an imaging device using this type of photocathode. Accordingly a 12-month program of exploration of transmission photocathodes and their incorporation in sealed off tubes was proposed, with the important proviso that, owing to the difficulties foreseen and unforeseen in development of transmission 3-5 cathodes, a backup program should be incorporated for developing tube designs utilizing front surface operation of the photocathode. In the event, the work statement provided for the development of the transmission design of tube only, which turned out to represent a technological tour de force far exceeding the time and resources available. In addition however, the timetables of the programs making use of this development turned out to require deliveries some six months after the beginning of the program,

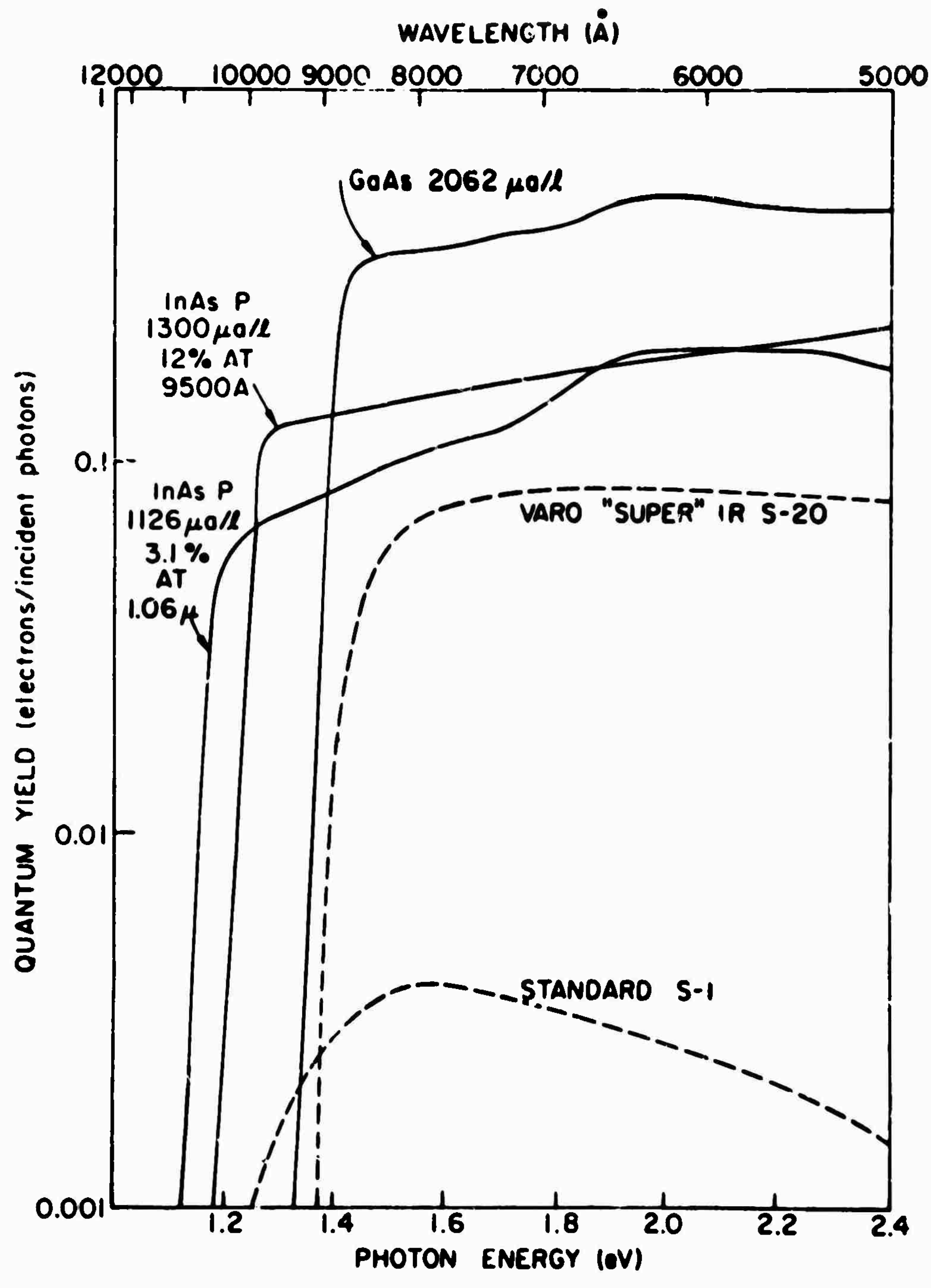

WAVELENGTH (Å)
12000
10000
9000
8000
7000
6000
5000
GaAs 2062 μa/l
InAs P
1300μa/l
12% AT
9500A
InAs P
1126μa/l
3.1%
AT
1.06μ
VARO "SUPER" IR S-20
STANDARD S-1
QUANTUM YIELD (electrons/incident photons)
0.1
0.01
0.001
1.2
1.4
1.6
1.8
2.0
2.2
2.4
PHOTON ENERGY (eV)

Figure 1

rather than the 12 months envisaged. This implied exclusive concentration on one single available cathode technology, namely growth of thin layer InAsP cathodes on InP substrates, to the exclusion of investigation of other possibilities. Not surprisingly, the limited funds available were rapidly exhausted in attempting to meet the compressed schedule by a frontal assault on the objectives, and also not surprisingly, the hardware finally shipped has fallen far short of the goals in respect of quantum efficiency, noise level, and image quality. The highest 0.965 micron quantum efficiency observed in transmission has been 3%, and the highest value shipped in sealed-off tubes has been 1.5% (at -68°C), against a theoretical maximum expectation between 3% and 8%, depending on parameters assumed. Theoretical expectations will be discussed in detail in the next section.

The noise levels in the tubes shipped appear to be due, not to thermionic emission, but to cathodoluminescence of the internal surfaces of the tube which, since the vacuum surface of the cathodes are of unprecedented sensitivity to white light (see Table I), can excite large photocurrents indistinguishable from thermionic emission. The general internal cathodoluminescence appears to be excited by field-emitted electrons from the metallic structures surrounding the cathode, whose work functions are drastically lowered during the (Cs,O) activation of the cathode. Thus no appreciable improvement in background noise is expected on cooling to dry ice temperatures, as would result if the noise currents were due to thermionic emission.

TABLE I

Cathodes for Contract N00014-71-C-0073

Sample #	Opaque Sensitivity White Light (a)	IR (b)	1.25 (c)	1.3 (d)	Semitransparent 1.25	Bandgap	Notes
1-21-A	854	76	3.6	6.7		1.27	
1-25-A	485	36	1.4	3.8		1.27	
1-26-A	553	33	1.1	3.2		1.27	
1-27-A	935	89	3.9	8.8		1.28	
1-27-B	977	90	4	8.7		1.28	
1-28-A	649	52	2.0	5.4		1.29	
1-1-A	1082	86	3.8	8.2		1.28	
1-10-B					~0.6		Processed in INV #7
1-11-A	1095	99	4.9	9		1.26	
1-16-B	932	85	4.8	7.6	1	1.25	19 μm thick
1-16-B*	1178	108	5.3	9.7	1.1	1.25	
1-19-B	690	50	1.8	4.9	1.1	1.26	
1-24-B					0.77		Processed in INV #7
1-26-A	496	44	2.3	3.7		1.25	
1-4 -A	1070	93	4.4	8.5		1.25	
1-4-A*	998	84	4	7.4		1.25	
1-4-D	894	70	2.7	7	1.1	1.26	
1-4-D*	793	56	2.1	5.5		1.26	
1-5-C					1		Processed in INV #7
1-10-B	542	21	0.32	0.95		1.33	
1-11-D	704	57	3	4.7	0.99	1.25	1.8 μm thick
1-15-B	495	23	0.67	2.3	1.1	1.29	InP p^+ interface
1-16-B	700	63	3.4	5.6	3	1.25	
1-16-B*	775	65	3.1	6.0	2.1	1.25	
1-16-B†					0.4		Processed in INV #8
1-29-A					0.67		" " " #8
1-6-C					1.5		" " " #9
1-12-A					1		" " " #8

Polished.

Second polish.

(a) μ A/lumen
(b) μ A/lumen through R filter
(c) quantum efficiency at 1.25 eV
(d) at 1.3 eV

TABLE I (Contd.)

Sample #	Opaque Sensitivity White Light [(a)]	IR [(b)]	1.25 [(c)]	1.3 [(d)]	Semitransparent 1.25	Bandgap	Notes
41-12-B					~ 0		Processed in INV #9
41-14-B					0.25		" " " #10
41-15-A					1.5		" " " #10
41-16-A					3		" " " #9
41-19-A					0.4		" " " #11
41-21-A					1.7		" " " #12
41-21-B					2.3		" " " #11
41-21-B*					0.5		" " " #12
41-26-A					2.1		" " " #11
41-28-A					1		" " " #12
41-29-A					2.6		" " " #13
51-3-A					0.67		" " " #13
51-7-A	490				1		Transfer to INV #12
51-11-C	900	68					Processed in diode
51-13-A					1.3		Processed in INV #14
51-14-A					1.7		" " " #13
51-18-A					~ 0		" " " #14
51-18-A†	110						In preprocessor
51-21-A					0.12		Processed in INV #15
51-21-B	≥500				1		" " " #14
51-25-A	250						In preprocessor
51-27-A	≥600				2		Transfer to INV #16
51-28-A	≥780						Dropped
61-2-B	680						Dropped
61-3-A	≥575				1.3		Transfer to INV #16
61-4-A	700	60					" " " #15
61-8-A					1.9		Processed in INV #1
61-10-A	560	47			1		Transfer to INV #17
61-17-A	700				1.5		" " " #18
61-28-A	560				0.6		" " " #19
61-30-A	≥800				2.7		" " " #19

* Polished.
† Redone.

TABLE I (Contd.)

ample #	Opaque Sensitivity White Light (a)	IR (b)	1.25(c)	1.3 (d)	Semitrans-parent 1.25	Bandgap	Notes
1-30-B	400				0.6		In preprocessor
1-7-A	790				2		Transfer to INV #18
1-13-A	650				1		" " " #20
1-21-A	1000	98			1.5		" " " diode#1
1-29-B	860	86			2.6		" " " #21
1-6-A	840	78			1.8		" " " #22
1-31-A	≥800	~ 80			1		" " " #24

59 total samples

40 total activations in tubes

It is evident that the technology of transmission 3-5 photocathodes themselves, and of special image tube technology that they require for satisfactory operation, have far to go. Nevertheless, a number of lessons were learned from this program. Those involving technology are described in more detail below.

PHOTOCATHODES

As is well known by now,[3-5] very high performance can be obtained from appropriately designed 3-5 ternary photosurfaces activated with cesium and oxygen. Important parameters are a long diffusion length L in the p-type 3-5 photosensitive layer, a high surface escape probability P for electrons which diffuse to the surface region (the edge of the surface depletion layer) and in the case of transmission cathodes, a low recombination velocity S at the interface between the epitaxial photosensitive layer and the transparent substrate on which it is grown.

The escape probability is maximized by securing a narrow depletion region at the surface by heavy p-type doping, and by lowering the vacuum energy level below that of the conduction band in the bulk of the 3-5 layer, by application of a thin activation layer. No other activator has been discovered that can match (Cs,O) in effectiveness--the favorable performance observed with (Cs,F) activation[6,7] is believed to be attributable to oxygen contamination. Even with (Cs,O) the threshold for efficient performance (quantum efficiencies in excess of 1%) lies at about 1.1 microns (or roughly 1.1 eV) owing to an interfacial energy barrier[4] between the 3-5 ternary (InAsP and InGaAs have been intensively investigated so far) and the activation layer, over which electrons must make their way in order to escape into vacuum. The barrier height is determined by interactions between the surface electronic states of the 3-5 ternary and electronic states of the activation layer.

A significant lowering of the barrier by other combinations of 3-5 and activator is not ruled out. However, many have been tried both at Varian and elsewhere, without any indication of improvement over InAsP (Cs,O). Interfacial barrier effects significantly interfere with the performance of cathodes designed for 0.965 micron operation, resulting in escape probabilities of 10% to 15% under carefully optimized conditions, and lower values under adverse conditions found in operational devices. James[8] has made some numerical estimates of the performance of complete transmission cathodes using escape probabilities[9] and other parameters appropriate for InAsP alloys. The results are reproduced as Figs. 2 through 5, which are for a photon energy of 1.25 eV or approximately the wavelength of interest here. It is clear that for a good interface (S=0) the optimum thicknesses of the order of the electron diffusion length L, whereas for a poor interface (S=∞) the optimum thicknesses are somewhat greater. Diffusion lengths of approximately 2 microns had been measured on longer wavelength cathodes using InAsP alloys. The fabrication problem therefore is to produce a 2-micron thick film of InAsP with "bulk" perfection on some transparent heteroepitaxial substrate. InP was chosen, as a reasonably close lattice match to InAsP alloys of appropriate bandgap, and reasonably transparent to 0.965 micron radiation (Fig. 6).

Half-inch diameter substrates were obtained from the RRE Electronic Materials Facility and Zn-doped InAsP layers of appropriate bandgap, acceptor density, and thickness grown on these by liquid phase epitaxy.[10] In order to minimize reflective loss from the substrate,

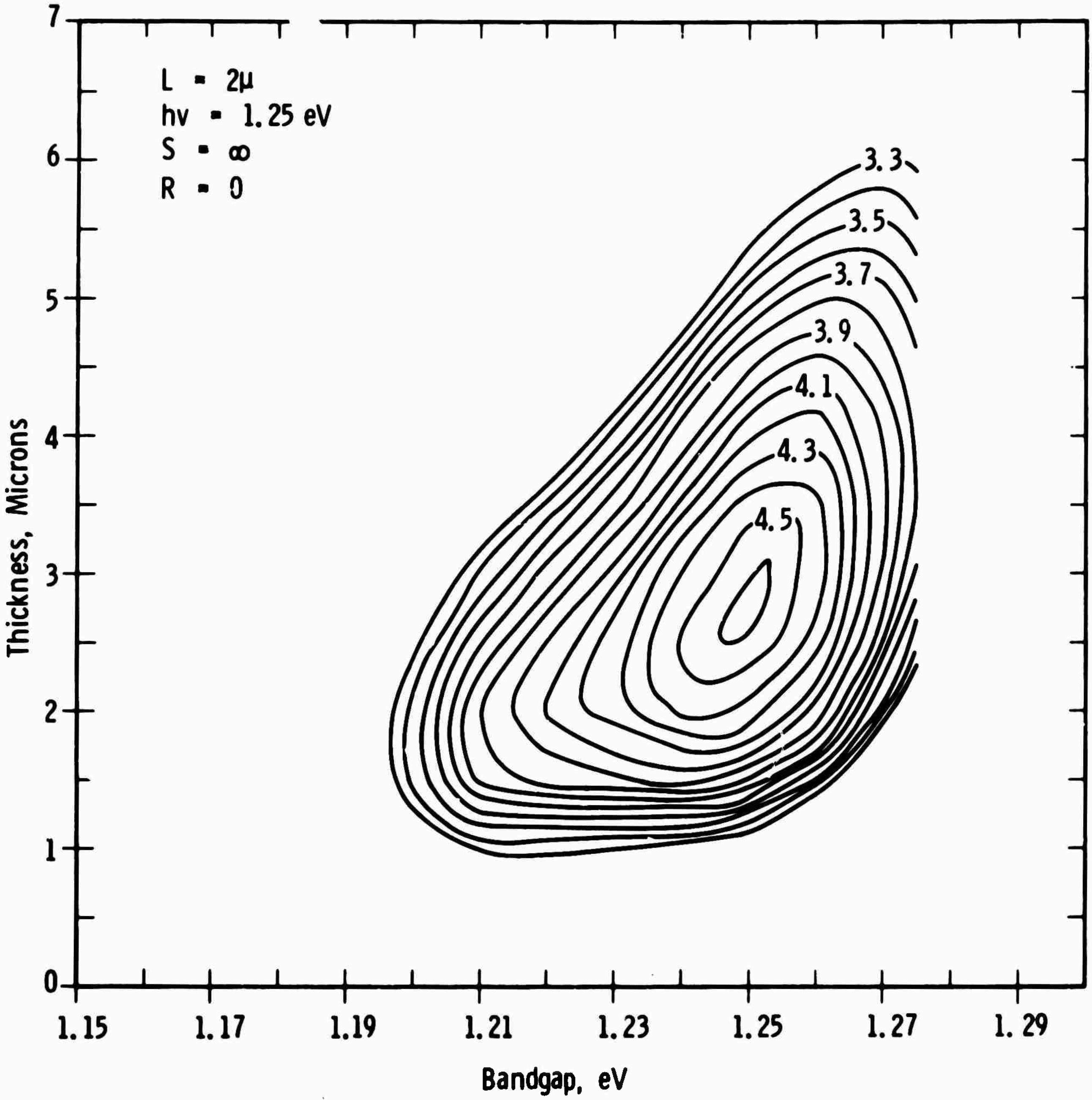


Figure 2 . Constant Transmission Yield Contours for Liquid Epitaxial InAsP Activated with Cs_2O, for a Photon Energy of 1.25 eV and an Infinite Interfacial Recombination Velocity. An optical matching layer (R = 0) on the back surface is assumed. The constant yield contours are shown every 0.1% from 3.3% to 4.6%.

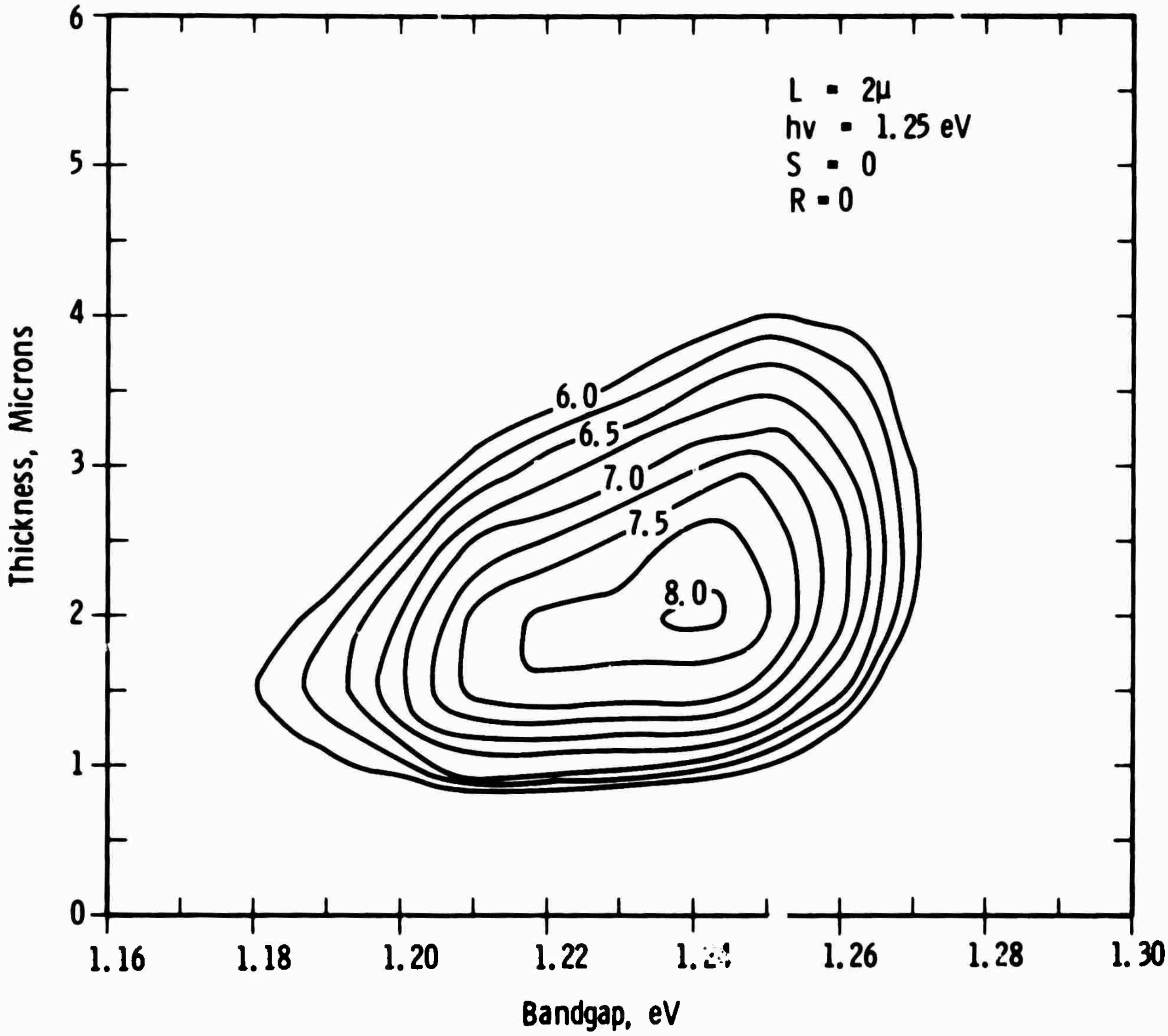


Figure 3. Constant Transmission Yield Contours for Liquid Epitaxial InAsP Activated with Cs_2O, for a Photon Energy of 1.25 eV and a Zero Interfacial Recombination Velocity. An optical matching layer (R = 0) on the back surface is assumed. The constant yield contours are shown every 0.25% from 6.0% to 8.0%.

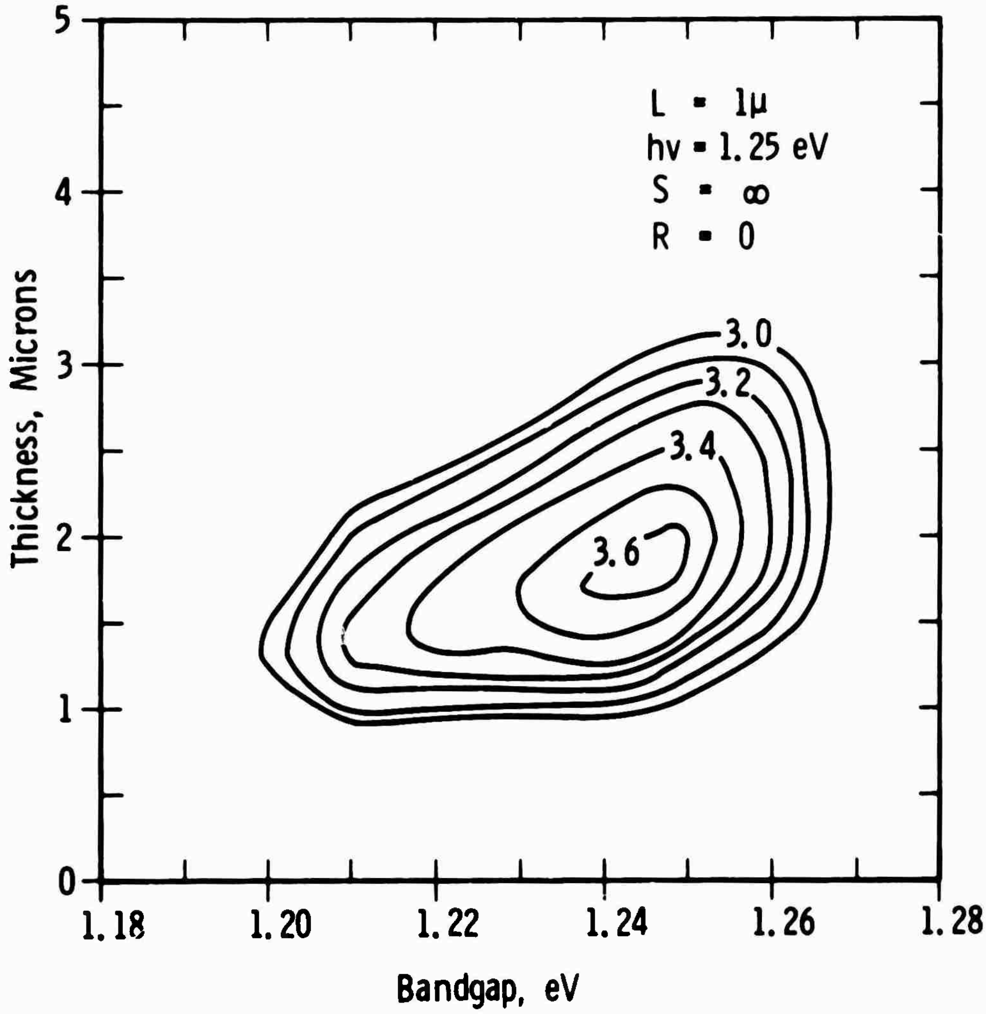


Figure 4. Constant Transmission Yield Contours for the Same Case as Figure 13, Except for a Diffusion Length of 1 Micron. Contours are shown every 0.1% from 3.0% to 3.6%.

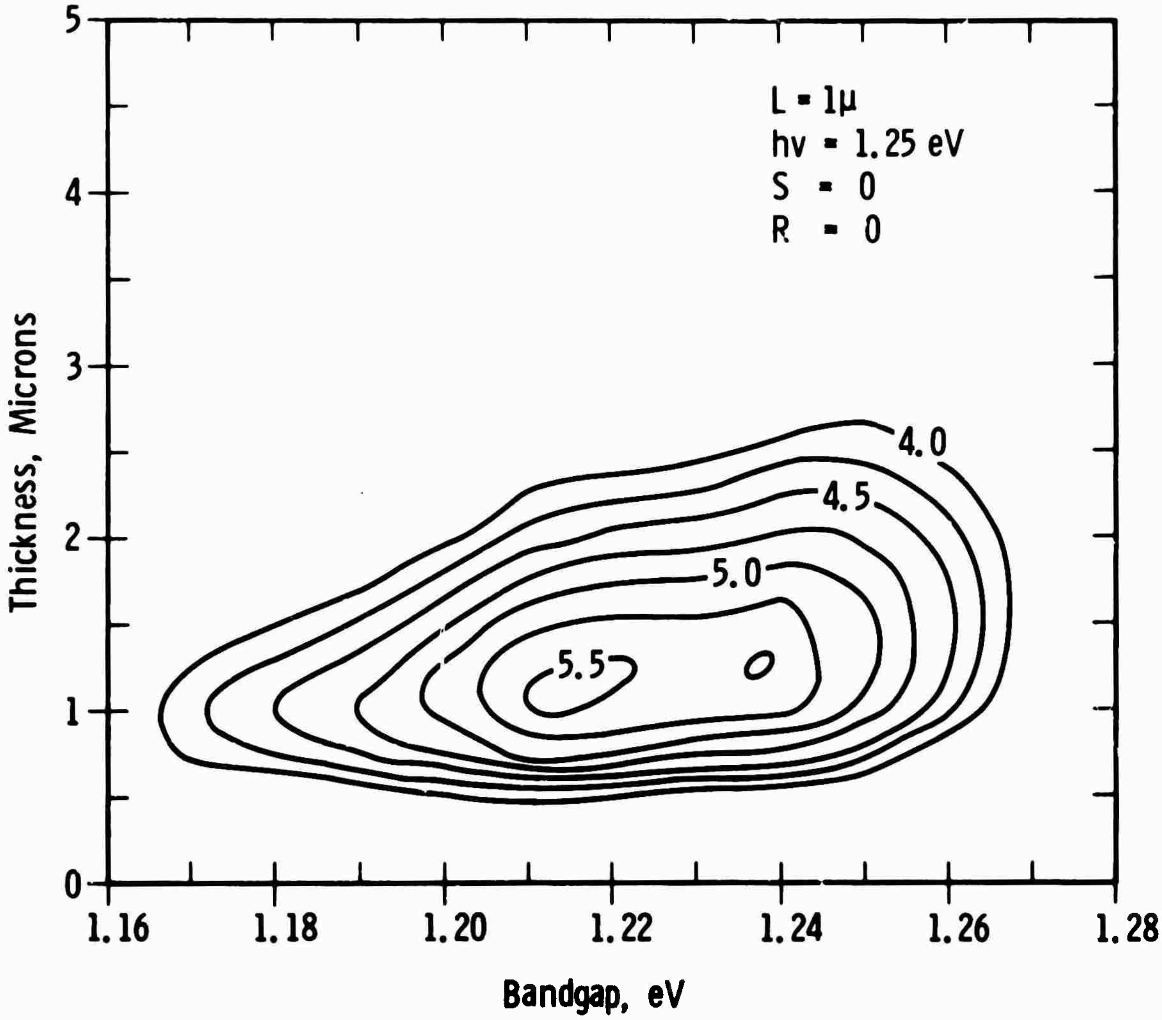
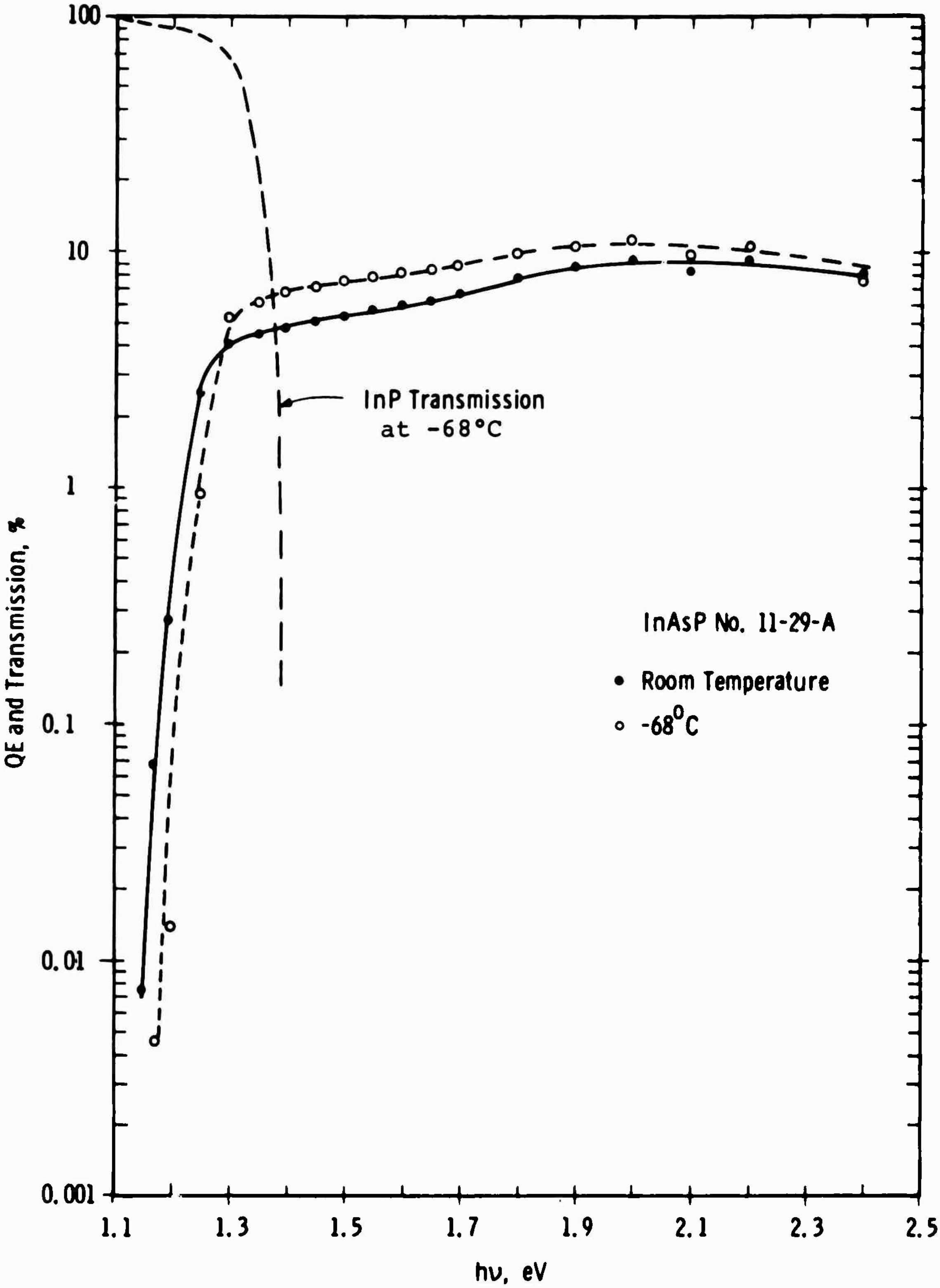


Figure 5. Constant Transmission Yield Contours for the Same Case as Figure 14, Except for a Diffusion Length of 1 Micron. Contours are shown every 0.25% from 4.0% to 5.5%.



100
10
1
0.1
0.01
0.001
QE and Transmission, %
1.1
1.3
1.5
1.7
1.9
2.1
2.3
2.5
hν, eV
InP Transmission
at -68°C
InAsP No. 11-29-A
Room Temperature
-68°C

Figure 6

typically 30%, the back surface of the InP substrate disc was coated with an optical matching layer of sputtered SiO_2, before growth. The loss of light due to absorption in the substrate (Fig. 6) remains, however.

The previous work referred to had tended to indicate a low recombination velocity with the InAsP/InP system. This indication was spurious, owing to inaccurate evaluation of experimental results, and the present program has indicated a large S value for the InAsP/InP interface. For $S=\infty$, the calculated maximum value of quantum efficiency (Fig. 2) is 4.6% for an optimized layer thickness of just under 3 microns, with a material of bandgap 1.25 eV giving a diffusion length of 2 microns. For a diffusion length of 1 micron (Fig. 4), the maximum quantum efficiency expected is 3.6%, the optimum thickness is approximately 2 microns and the optimum bandgap 1.24 eV. According to Fig. 3, a low recombination interface with a diffusion length of 2 microns would generate a maximum quantum efficiency of 8% in a 2-micron thick layer with a bandgap of 1.24 eV. The experimental observation of higher values than those quoted in front surface operation (Fig. 1) is an indication of excellent diffusion lengths in the thick layers used for those measurements. The requirement for very thin layers in a heteroepitaxial situation leads to more or less complete determination of the minority carrier lifetime by the high density of dislocations in the layer, necessitated by accommodation of the InAsP lattice to the InP lattice spacing in the growing layer. As already mentioned, there was no opportunity on this program to try out systems which might have generated more favorable conditions.

As can be seen from Fig. 2, it is easy to stray from optimum conditions of bandgap and thickness, in growth of the photocathode. Further, in fabrication of operational tubes, less than optimum activation may result from processing difficulties, and poorly understood chemical interactions of the reactive activation materials (Cs,O) with essential elements of the tube (particularly phosphor screens). Tube technology is discussed in a later section. The net result of substrate absorption, high recombination velocity, low diffusion length, incorrect layer bandgaps and thicknesses, and hostile tube environments causing declines in sensitivity after seal-off, has been to generate performance close to 1% quantum efficiency in tubes delivered under this program. A histogram of performance for cathodes activated under this program (Fig. 7) show a statistical distribution with a maximum around 1%, and a tail significantly populated at the 3% level.

Table I lists white light sensitivity, with and without an infrared filter, quantum efficiency at 1.25 and 1.3 eV, transmission yield, bandgap and fate of the cathodes activated under this program. Figure 8 compares the front surface and transmission yields of one of the best of these.

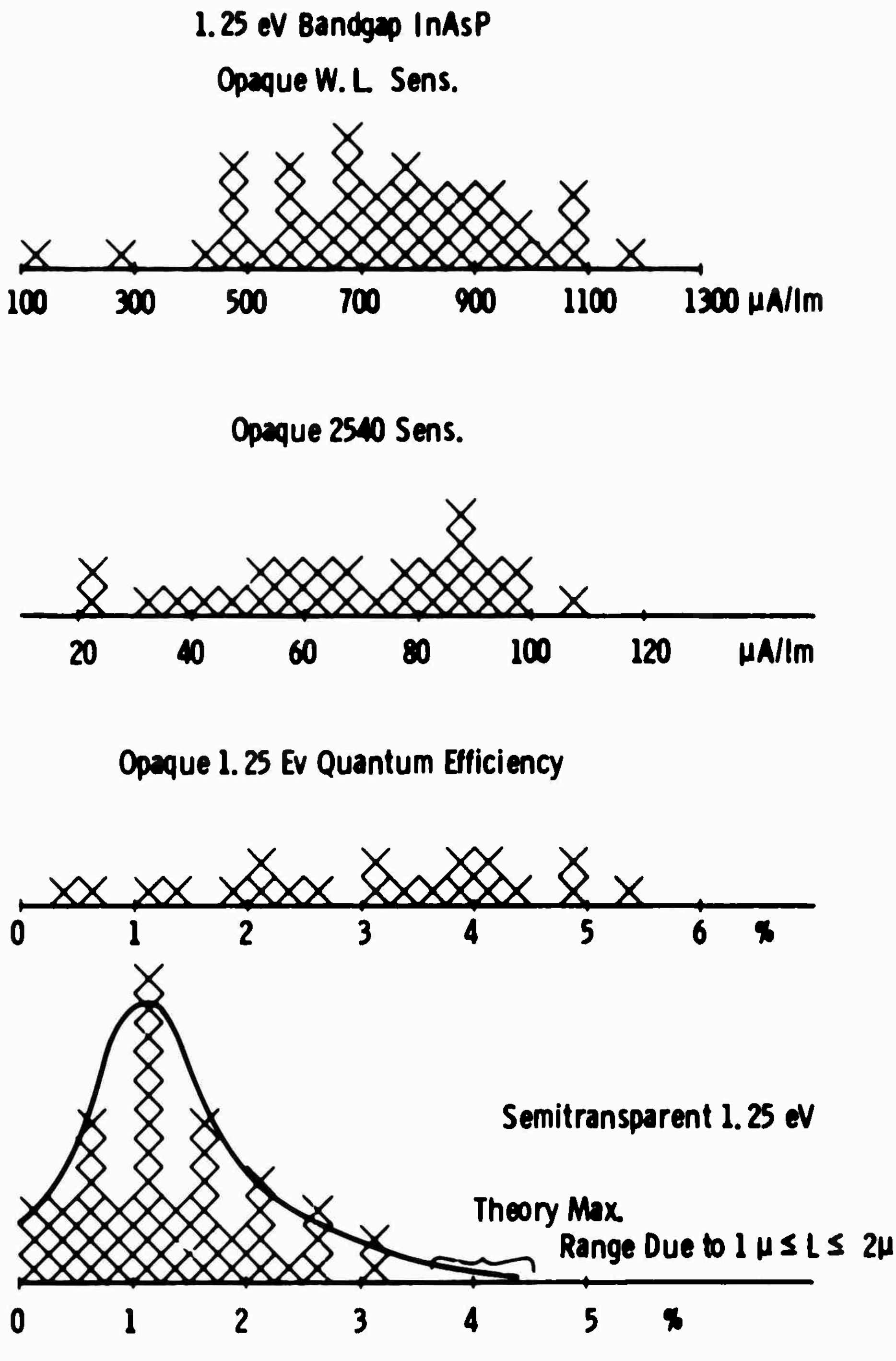
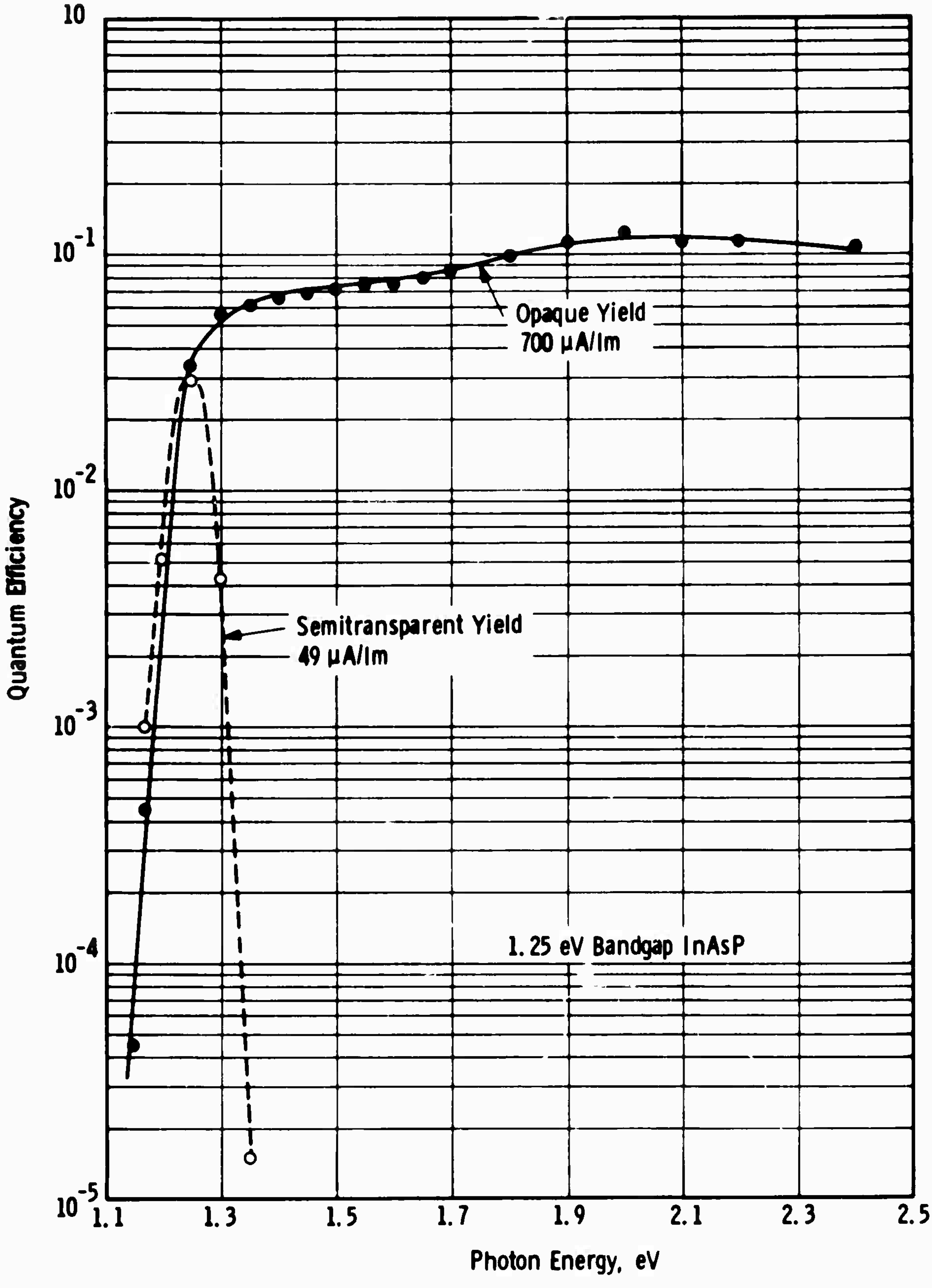

1.25 eV Bandgap InAsP
Opaque W. L. Sens.
100 300 500 700 900 1100 1300 μA/lm
Opaque 2540 Sens.
20 40 60 80 100 120 μA/lm
Opaque 1.25 Ev Quantum Efficiency
0 1 2 3 4 5 6 %
Semitransparent 1.25 eV
Theory Max.
Range Due to 1 μ ≤ L ≤ 2μ
0 1 2 3 4 5 %

Figure 7



10
10^-1
10^-2
10^-3
10^-4
10^-5
Quantum Efficiency
Opaque Yield
700 μA/lm
Semitransparent Yield
49 μA/lm
1.25 eV Bandgap InAsP
1.1
1.3
1.5
1.7
1.9
2.1
2.3
2.5
Photon Energy, eV

Figure 8

IMAGE TUBE

In order to meet the requirement of transmission operation of the cathode and to minimize the interactions of the cathode with other elements of the tube, a flat cathode inverter tube design (Fig. 9) was adopted. This incorporates an electron-optical distortion corrector in the screen space which also forms part of an ion trap. The tube can be gated by applying negative bias to the focus electrode surrounding the cathode.

The optimum processing schedule has been found to go as follows. The tube is attached to the pump station via a wide-bore pumping tubulation through which the cathode can ultimately be inserted into its holder in the tube (Fig. 10). The tube is baked out at 400°C for 24 hours, and an alkali cathode formed on the input window. This is excited by an ultraviolet source and the internal surfaces of the tube "electron scrubbed" for 12 hours. (The phosphor screen is subjected to prolonged electron scrubbing as a final stage in its preparation before being mounted in the tube.) The alkali cathode is then baked out. A 3-5 cathode is inserted via a vacuum interlock into the main chamber of the pump, where it is heat-cleaned before being transferred into the tube through the pumping tubulation. The cathode is then activated with a (Cs,O) codeposition. Oxygen is leaked into the tube via a heated silver tube, which is subsequently squeezed off, and Cs is generated by conventional chromate-silicon "channels." Optimum activation is not at first maintained, owing to slow equilibration of the Cs and O with other elements of the tube, and needs to be restored with fractional monolayer additions of Cs_2 and/or O_2.

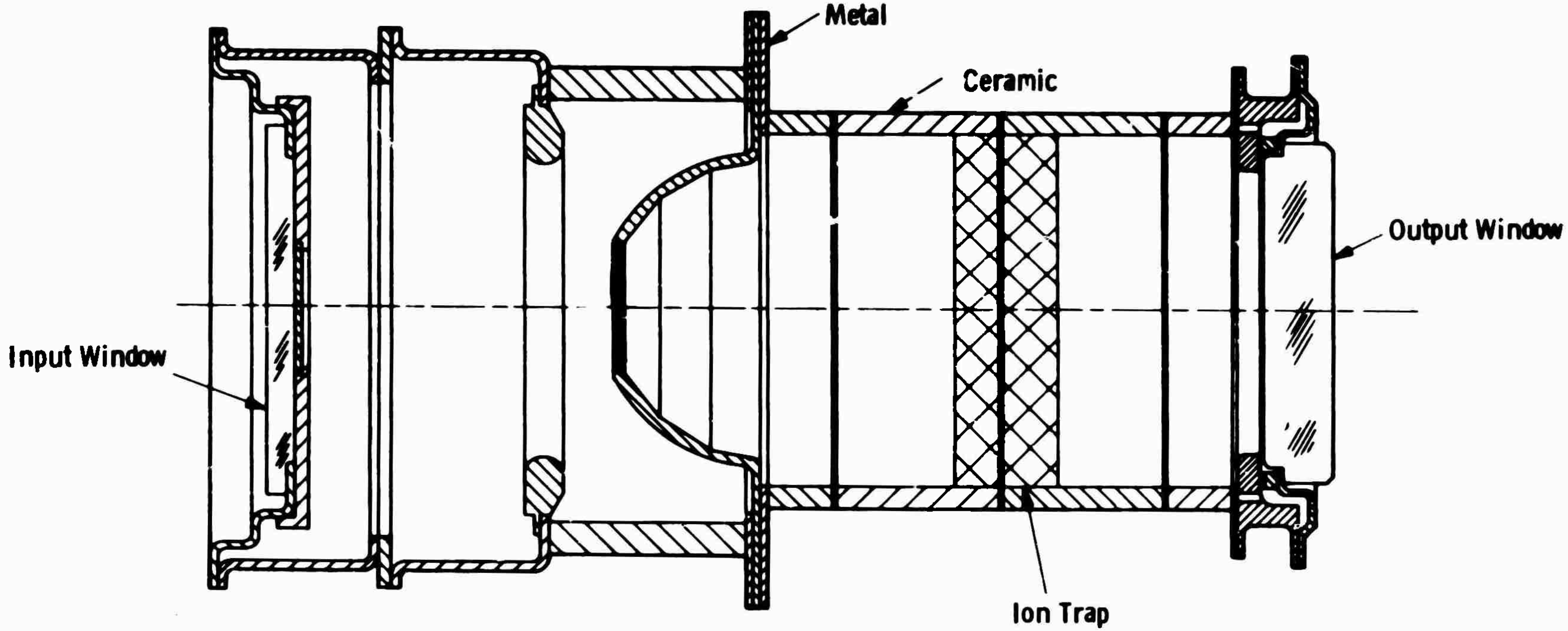


Figure 9

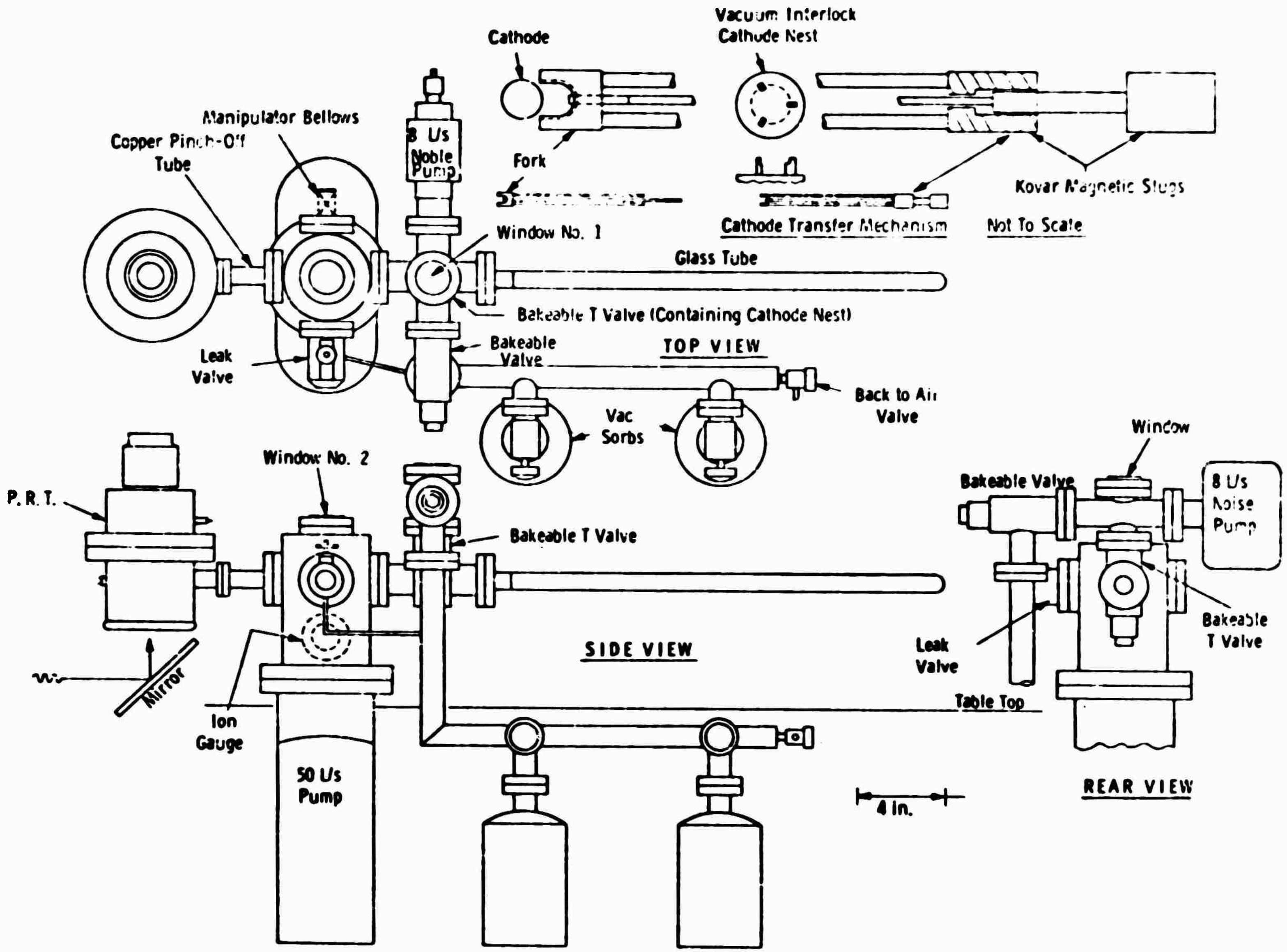


Figure 10. Interlock Tube Processing System.

The period of this drift eventually becomes of the order of weeks, after which the tube is sealed off. Under such circumstances, the cathode is susceptible to poisoning by partial pressures of CO or CH_4 for example (or even Cs, O, or OH radicals) of 10^{-13} or 10^{-14} Torr, which cannot readily or unambiguously be identified or traced back to source. This slow instability of low threshold cathodes, which does not occur with GaAs cathodes, has been a major problem under this program.

IMAGE TUBE PERFORMANCE

Four experimental tubes were shipped, as required by the contract. An early sample went to Sylvania Electronic Systems Group and later samples to Airborne Instruments. The best cathode performance observed is shown in Fig. 8, 3% quantum efficiency at 1.25 eV in transmission, and a front surface yield of 700 μA/lm. Cathodes sealed off in tubes averaged between 1.0 and 1.5% at 1.25 eV (and -68°C). This is a factor of ten higher than available from conventional photocathodes. No extensive investigation of background noise was undertaken, since the tube fabrication effort overexpended the available funds. It appears that the background is not due to thermionic emission but to photoemission excited by internal luminescence. Internal luminescence could be excited by leakage currents through the bulk or over the surface of insulators or by electron bombardment of internal surfaces by electrons field emitted from the cathode holder or focus electrode. This type of background would be relatively unaffected by cooling of the tube, as observed by Sylvania.[2] The comment of Ref. 2 on the difficulty of gating this tube is not understood. The electrode system is of a ceramic/metal disc seal-type which should support extremely high currents. Further discussion of the comments in Ref. 2 on the performance of this interim tube is hardly relevant, since the tube had clearly been damaged by an overvoltage.

Qualitative resolution measurements on this type of tube showed limiting resolutions of the order of 50 line pairs/mm at the center of the cathode, and 30 near the edge. These are significantly lower than calculated for the electron optics, and are believed to be due to light scattering in the cathode/substrate combination.

CONCLUSIONS

As regards 3-5 photocathodes, the difficulties inherent in the development of transmission types, well known to those involved in the art, are illustrated in this program--the necessity for a heteroepitaxial interface to the transparent substrate implies a high recombination velocity there, unless favorable growth conditions can be selected, and the necessity for a thin active layer grown on a lattice-mismatched substrate implies a heavily dislocated crystal and poor minority carrier lifetime, again unless favorable combinations of layer and substrate can be used. It appears that when these problems are solved, a quantum efficiency of 8-10% at 0.965 microns in transmission can be anticipated for the InAsP (Cs,O) system.

Stability of the cathode and low background noise will require further development of tube technology.

REFERENCES

1. W. Chiou and F. Pace, "Research on Imaging Properties of Optical Parametric Upconverter," Final Report on N00014-70-C-0161, AIL Div. of Cutler Hammer, July 1971.

2. J. Falk and J. M. Yarborough, "Ten micron wideband detector," Final Report on N00014-70-C-0224, GTE Sylvania, Inc., September 1971.

3. R. L. Bell and W. E. Spicer, Proc. IEEE, 58, 1788 (1970).

4. L. W. James et al., J. Appl. Phys. 42, 580 (1971).

5. R. L. Bell et al., "Interfacial Barrier Effects in 3-5 Photoemitters," Appl. Phys. Letters, to be published.

6. J. J. Uebbing and R. L. Bell, Proc. IEEE, 56, 1624 (1968).

7. S. Garbe, Phys. Stat. Sol. (a) 2, 497 (1970).

8. Quarterly Progress Report No. 8 on contract DAAK02-69-C-0420, April 1971.

9. L. W. James et al., "III-V Ternary Photocathodes," Gallium Arsenide and Related Compounds (Conf. Series #9, IPPS, London, 1971), p. 195.

10. G. A. Antypas and T. Yep, J. Appl. Phys. 42, 3201 (1971).