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CONTRACT: SERI XP-9-8081-1
"Materials for High Efficiency Monolithic Multigap Concentrator Solar Cells"
March 1981

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The objectives of this work are to develop a materials technology of the AlGaInAs and AlInAsSb mixed crystal systems. These technologies are directed towards the development of a two-gap, monolithic, lattice-matched concentrator cell with 28% or higher AM2 conversion efficiency at 500 to 1000 suns.

The work to be performed is subdivided into the five major tasks outlined below.

Task 1: Develop and demonstrate the technology for a grading layer of GaInAs/GaAs and low-bandgap cells in AlGaInAs/GaInAs/GaAs.

Task 2: Develop and demonstrate intercell tunnel junction contacts in the higher bandgap AlGaInAs alloys.

Task 3: Develop and demonstrate technology for a higher bandgap concentrator cell in AlGaInAs alloys.

Task 4: Demonstrate a complete two-gap monolithic concentrator cell with AM2 efficiency of 28% or more.

Task 5: Investigate the potential of AlInAsSb alloys grown on InAs substrates.

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Short Summary

The progress made on the above tasks is summarized below.

Task 1: Background doping of layers grown from trimethylarsenic is improved. A series of studies is described to evaluate the performance of the 1.15-eV GaInAs junction as a function of grading routine. The photoresponse of the junction is substantially improved. Problems with trimethylindium control were identified and solved.

Task 2: Several aspects necessary for OM-VPE-grown interconnects were studied, including increased growth rate of GaAs and the evaluation of new dopants. A new interconnect is discussed which uses a layer of evaporated metal to electrically interconnect the top and bottom cell.

Task 3: Extensive correlation between the crystal composition and input fluxes has been made for AlGaInAs. Good photoluminescence and photoresponse is demonstrated for $Al_{.2}Ga_{.8}As$.

Task 4: Progress on Tasks 1, 2, and 3 is sufficient so that work on an all-OM-VPE-grown cascade cell is underway. The cell will initially be demonstrated with a GaAs bottom junction and an $Al_{.2}Ga_{.8}As$ top junction.

Task 5: Because of the heavy attention devoted to Tasks 1, 2, 3, and 4, work on this task has been deferred.

DETAILED DISCUSSION

Task 1:

A. Doping

Previously, it was reported that it is necessary to use an alternate arsenic source, trimethylarsenic (TMAs), to grow uniform good-quality GaInAs epitaxial layers.[1] However, the electrical quality of GaAs epitaxial layers grown from the alternate As source was inferior to layers grown with arsine. Typical backgrounds for GaAs layers grown with TMAs were found to be on the order of $\sim 10^{17} cm^{-3}$ n-type with associated room-temperature mobilities on the order of 2700 cm^2/V-sec.[2] Layers grown with arsine exhibit background dopings nearly two orders of magnitude lower with mobilities up to ten times that for the TMAs-grown crystals. The natural conclusion was that the backgrounds exhibited by GaInAs layers ($\sim 10^{17} cm^{-3}$, n-type) were also due to the use of TMAs.

Trimethylarsenic supplies have been purchased from two different suppliers: Alfa and Strem Chemicals. The electrical quality of layers grown with material from either supplier is comparable. During this period, a batch of TMAs purchased from Strem Chemicals was loaded into the reactor. This source produced the best quality layers yet obtained for TMAs-grown materials. Background dopings of GaAs layers were measured to be $4 \times 10^{16} cm^{-3}$ n-type with associated room-temperature mobilities on the order of 4000 cm^2/V-sec. This represents a significant improvement in both doping and mobility, as compared to previous results.

It is not clear if the improved electrical quality of the layers can be attributed to these new procedures or to improved material from the suppliers. A careful check on TMAs quality will be maintained in an attempt to identify impurities and the sources of the impurities. The quality of the TMAs is sufficient for high-quality solar cells, so additional distillation experiments will not be pursued at this time.

B. Grading and Junction Performance

Work during this period also continued on the study of grading procedures to reduce dislocations in the $Ga_{.8}In_{.2}As$ layers. Previous work relied on etch pit density (EPD) measurements to gauge the quality of the epitaxial layers.[2] Although EPDs provide a valid measure of dislocation density, the most important parameter from the standpoint of the multigap cell is the junction performance. Accordingly, a series of runs was undertaken to evaluate the effect of various grading routines on the 1.15-eV junction performance. A structure similar to Varian's GaAs/AlGaAs single-junction cell[3] was grown to evaluate the grading-junction relationship (Fig. 1).

The grading routines are illustrated graphically in Fig. 2. Two different steps (10 and 40 minutes) were examined for the 4% step-grading routine (b). Three different slopes were examined in the case of the continuous-grading procedure (c), which is composed of numerous discrete steps. The superlattice structure consists of a ramp, followed by 20 cycles of varying composition GaInAs layers, each about 100 Å thick. A 2-μm thick constant composition layer ($Ga_{.8}In_{.2}As$:Se) is grown immediately after the grading layers. This layer is followed by the remainder of the cell (Fig. 1).

The completed wafer was cleaved into pieces and rudimentary contacts alloyed to the substrate and cap layer. The photoresponse of the cell was measured, the cap etched, and the performance measured again. In all cases, removal of the absorbing cap layer improved junction efficiency.

Figure 3 illustrates the photoresponse for the structure with no grading layer. Junction response is improved by about 100 fold compared to the results reported in Quarterly Report No. 5. This is especially encouraging, since the structure is not optimized. It was

SCHEMATIC OF 1.15 eV TEST CELL

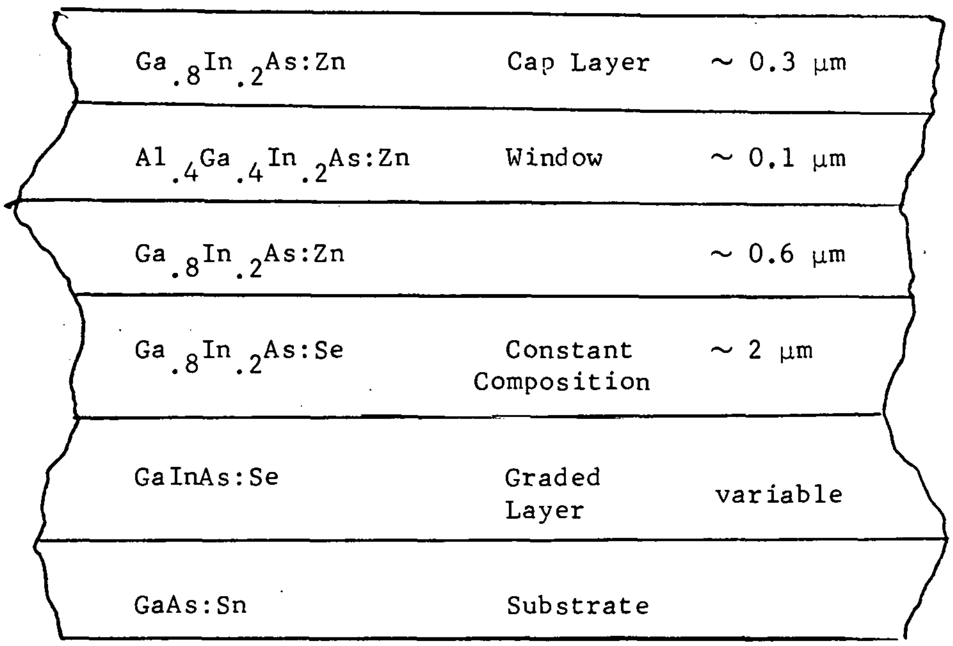
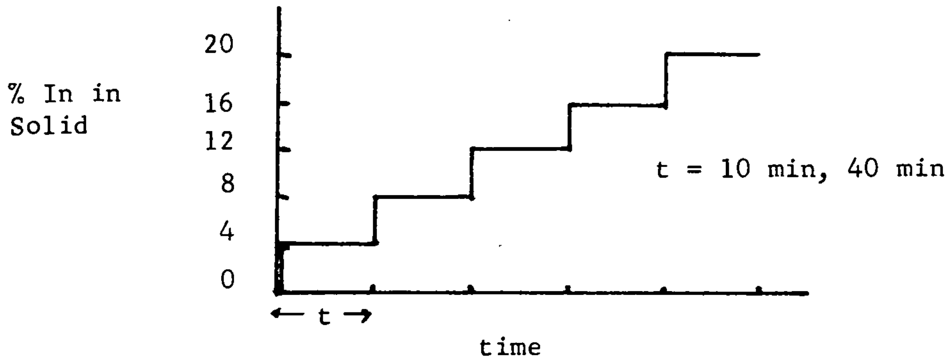


FIGURE 1

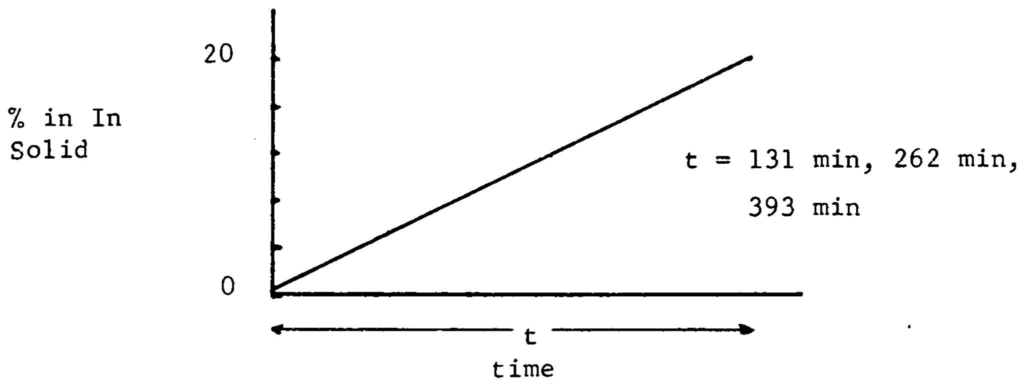
GRADING PROCEDURES

1. No Grading

2. Step Grading



3. Continuous Grading



4. Superlattice

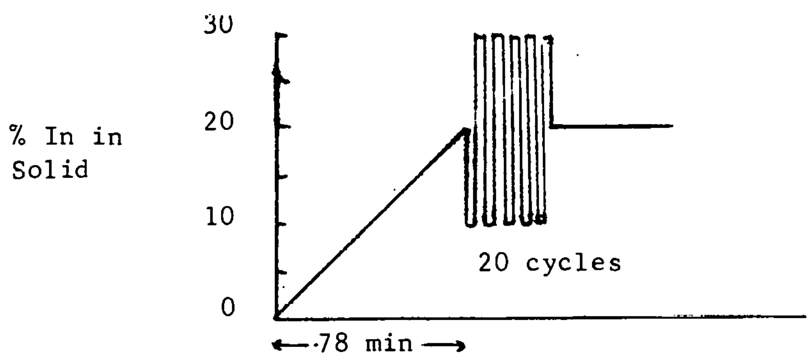
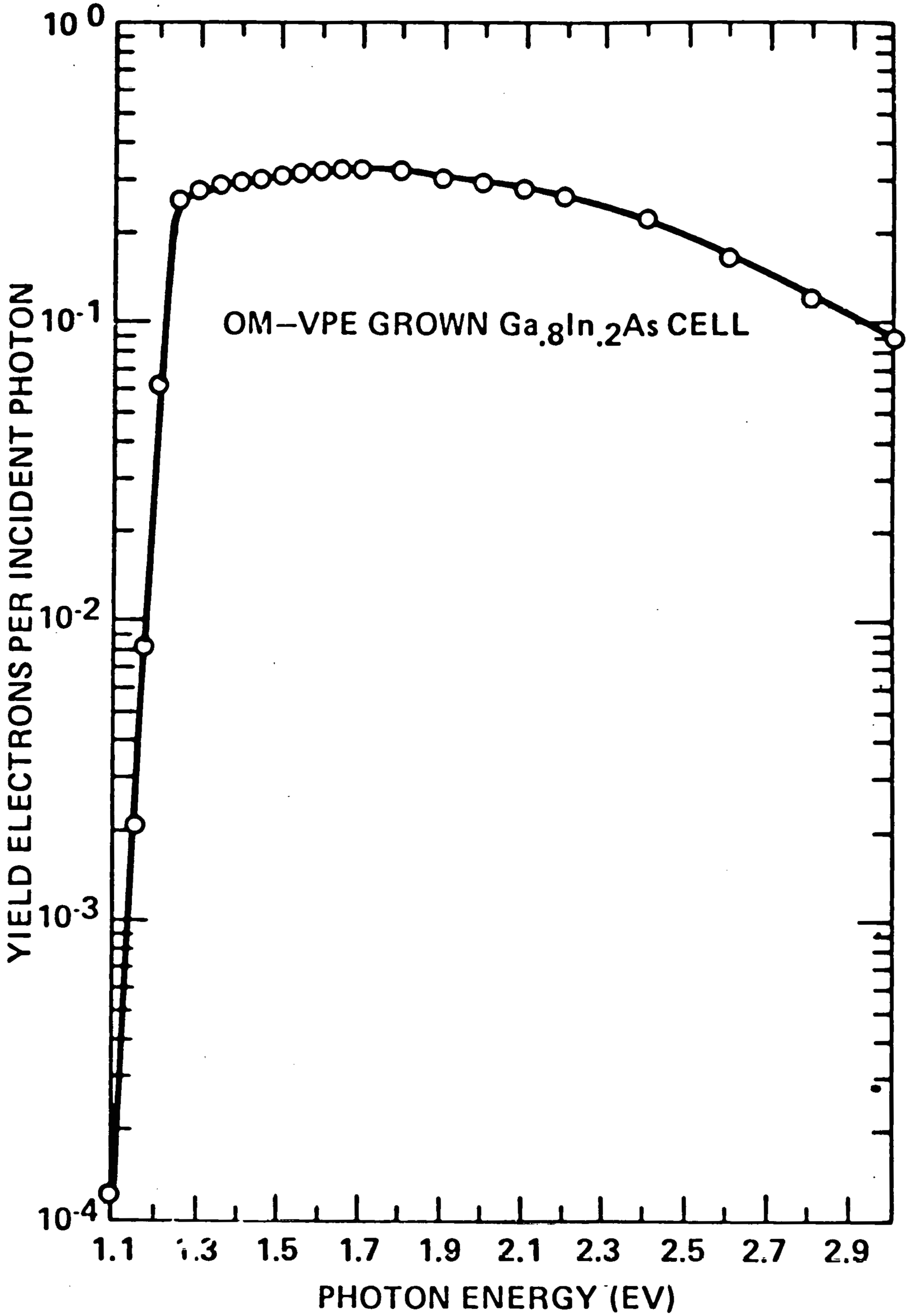


FIGURE 2



10 0
10-1
10-2
10-3
10-4
YIELD ELECTRONS PER INCIDENT PHOTON
OM—VPE GROWN Ga.8In.2As CELL
1.1
1.3
1.5
1.7
1.9
2.1
2.3
2.5
2.7
2.9
PHOTON ENERGY (EV)

FIGURE 3

expected that gains in the photoresponse could be realized by using various grading schemes to minimize dislocations in the $Ga_{.8}In_{.2}As$ layers. However, structures grown with grading layers (Fig. 2) showed no increase in efficiency. In most cases, the photoresponse was not as good as the structure with no grading layers.

The results were surprising, so careful thought was given to possible reasons for the anomaly. Two problem areas were identified: (1) doping and (2) variations in the GaInAs composition. Through this period there was difficulty with the stability of the H_2Se doping source. The low ppm mixtures are difficult to make and are not stable for long periods. Possibly low Se doping of the buffer and junction layer contributed to the poor photoresponse. However, a definite problem with GaInAs composition control was identified.

Photoluminescence measurements were performed on the solar cell structures to determine the composition of the top GaInAs layer. Since the same parameters were used for all growths, the same bandgap is expected for the layer. It was noted that the bandgap of the cap layer varied between 1.26 and 1.30 eV, corresponding to a drift in lattice constant between 5.70 Å and 5.72 Å. This is a significant variance, and since it is necessary to carefully control composition in order to gain the full benefit of grading routines,[4] it is likely that drift in the GaInAs composition contributed to the anomalous results of the performance. The growth rate of the GaInAs layers is very dependent on the composition of the alloy and decreases as the %In in the crystal increases. Therefore, the variation in composition of the layers will also result in growth rate variations. This may also represent a significant problem with respect to grading, since it is often necessary to carefully control the thickness of each grading layer as well as the composition.

Equipment changes were made to reduce the variation in GaInAs composition. Minor reactor design modifications were made to improve gas flow. This is expected to be a minor factor, however, compared to problems with the design of the TMIn sublimer. It was reported in previous reports that, above certain gas flow, the bubbler was not fully saturating the hydrogen stream with TMIn. It is now apparent that even at lower flows that the sublimer reproducibility is poor at best. This is most likely due to the changes in TMIn crystal morphology and surface area that occur during the temperature cycling that occurs in the bubbler. As the size and number of the crystals changes, it is not unreasonable that the degree in TMIn saturation might vary. Consequently, a new sublimer was designed. Essentially, the new system consists of a bulb containing the TMIn which is held at a fixed temperature. After the hydrogen is passed through the bulb, the gas stream is then passed through a condenser which is held at a lower temperature than the bulb. This causes a deposition of TMIn from the hydrogen stream and assures that the hydrogen stream is saturated for the TMIn vapor pressure at the temperature of the condenser coil.

A few runs were made with this new arrangement, but detailed data on reproducibility will not be available until the next period. It is expected, however, that substantially improved TMIn control will be achieved. This should allow rigorous compositional control required for the grading routines.

Plans for the next period include continued improvement of the TMIn control and then the question of grading routine versus junction quality will be attacked anew.

Parallel to the effort to improve TMIn flux control was an effort to increase the growth rate of the GaInAs layers. The standard input parameters result in a growth rate on the order of 0.03 μm/min. Presently, some of the grading routines take several hours to complete. Therefore, it is necessary to increase the growth rate while maintaining crystal quality, in order to be able to grow the proposed multijunction cells in a reasonable length of time.

Several runs were undertaken to investigate the relationship between growth rate and input flux. In the case of OM-VPE-grown GaAs,[5] a linear relationship is observed. The GaInAs studies indicated that a similar relationship is also observed between the input Group III flux and growth rate. A 25% increase in the TMGa and TMIn flux (at constant composition) results in approximately a 25% increase in the growth rate. Surface morphology exhibits no change within this range.

Further experimentation on increased growth rates was suspended pending the construction and testing of new sublimers that are capable of reproducibly saturating the hydrogen stream with TMIn.

Task 2: Interconnect Technology

The proposed multijunction structure calls for a shorted junction between the high and low bandgap cells. A tunnel junction is the most often proposed interconnect, but other shorted junctions should be considered. A multipronged approach to the interconnect problem was adopted. Investigation of OM-VPE-grown junctions continued with different structure and doping evaluations. In addition, work was carried out on a metallic-contact-shorted junction, with very promising results.

A. OM-VPE-Grown Interconnects

Several OM-VPE growths were performed aimed at producing a viable interconnect. The plan is to demonstrate a junction in GaAs and study the characteristics of this junction before attempting to grow the junction in the AlGaInAs layer proposed in the overall cascade cell structure. We reported previously[2] that a variety of p-on-n tunnel junction structures grown using Zn and Se as the dopants failed to exhibit tunneling. It was thought that the junctions were all too broad for tunneling, presumably due to the relatively high diffusion rate of Zn.

One way to reduce the Zn diffusion is to insure that the wafer is at the growth temperature for as short a period as possible. The limitation of this approach is that the thickness of the final epitaxial layer (GaAs:Zn) be too thin so that the contacts penetrate to the junction. Standard growth parameters require that the GaAs:Zn final layer takes several minutes to grow. If the growth rate were accelerated, then the time that the wafer is at high temperatures would be reduced, presumably with less Zn diffusion.

Numerous experiments were conducted aimed at exploring the accelerated growth rate of GaAs in the OM-VPE reactor. Standard growth rates were on the order of 0.08 μm/min, with an input of 50 micromoles/minute of TMGa. Figure 4 shows a linear relationship between the TMGa input flux and the growth rate of GaAs. This linear relationship is indicative of a mass transport-limited process which is consistent with previous studies.[6] More importantly for the interconnect work is that growth rates in excess of 0.5 μm/min can be obtained.

The doping of these accelerated growth rate epitaxial layers was also examined. Zinc doping of layers grown at the rate of 0.5 μm/min was examined, both for high and low zinc fluxes. At relatively low zinc fluxes, this resulted in doping levels of 10^{18} cm^{-3} p-type with associated room-temperature mobilities of 100 cm^2/V-sec. At higher zinc fluxes, doping levels in the range of 10^{19} carriers/cm^3 p-type were obtained. However, one of these samples exhibited a p-to-n type transition on cooling from 300°K to 77°K, while the other exhibited an n-to-p transition. This unusual behavior might result from defect mechanisms caused by the accelerated growth rate. The doping of the accelerated growth rate GaAs layers by H_2Se was also investigated. However, due to the stability problem of the H_2Se source, much of the data is suspect. Plans are to finish evaluating the Se doping and then to grow some tunnel junction structures at the accelerated rate in an attempt to sharpen the doping profile so that tunneling can be observed.

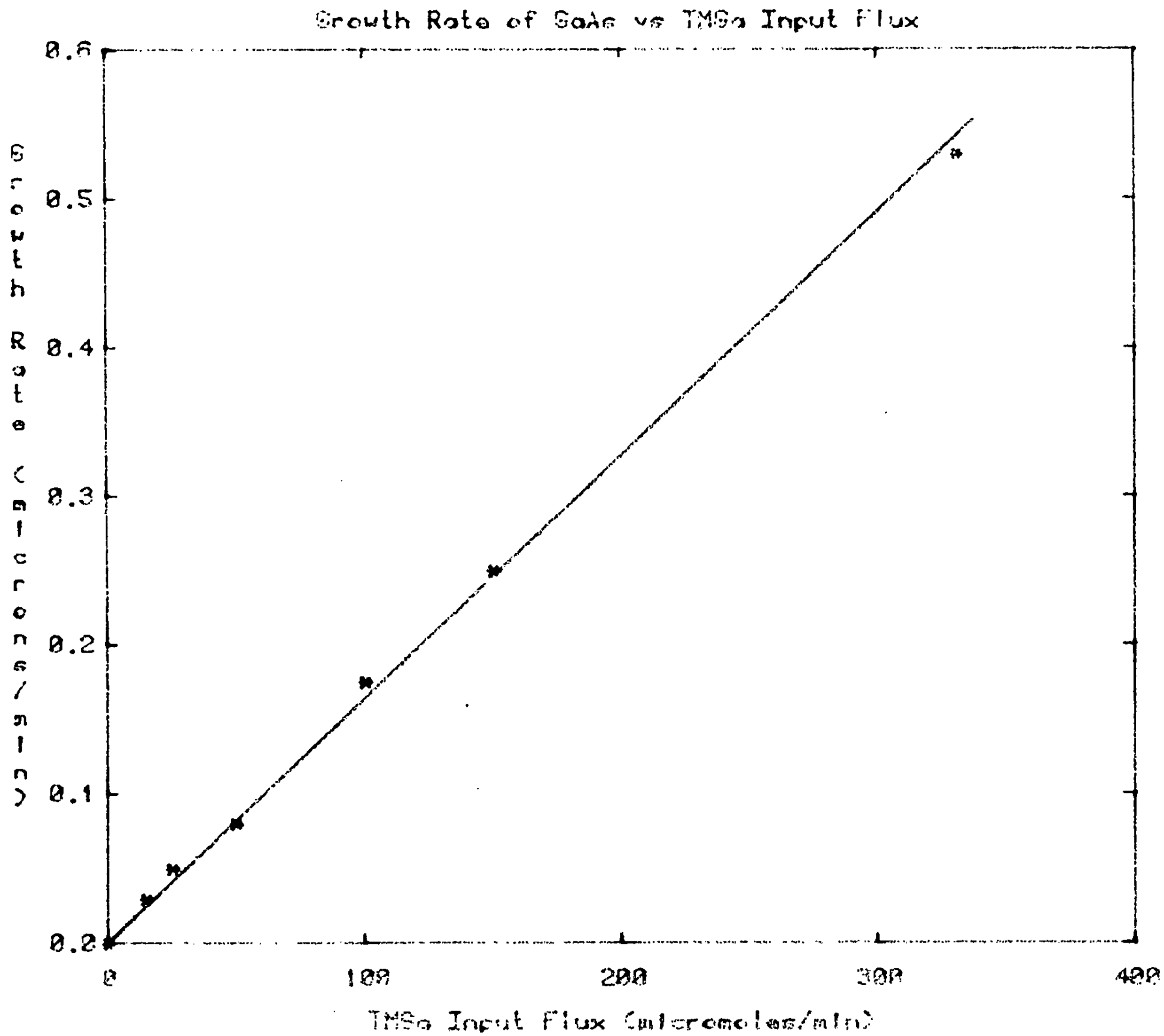

Growth Rate of GaAs vs TMGa Input Flux
Growth Rate (microns/min)
0.6
0.5
0.4
0.3
0.2
0.1
0.2
0
100
200
300
400
TMGa Input Flux (micromoles/min)

FIGURE 4

Magnesium is an ideal, slow-diffusing element for p-type doping in III-V materials, but the lack of volatile magnesium organometallics has precluded use of the metal in OM-VPE reactors. An experiment was performed in the OM-VPE system to use metallic Mg as the dopant source. A small Pyrex vessel was charged with a few grams of pure Mg and then wrapped with a heating tape and attached to the input link on the reactor. Magnesium has a fairly high vapor pressure at several hundred degrees C, so it was thought that passing a high rate of hydrogen through the heated pyrex vessel might introduce sufficient Mg to the reactor to produce P-type material. Unfortunately, even when several liters per minute of gas was passed over the heated Mg, no appreciable doping of a GaAs epitaxial layer was observed. Instead, all of the Mg condensed from the gas stream immediately upon entering the reactor.

Alternate n-type dopants were also studied during this period. Several GaAs growths were performed using tetramethyltin (TMSn) as the n-type dopant. Tin incorporates into the crystal to extremely high levels with no deterioration in crystal quality, as is observed for very high Se doping. Several tunnel junction structures consisting of GaAs:Sn substrate/GaAs:Sn/GaAs:Zn were grown and evaluated. It was found that even though the Zn-doped top layer was doped to above $10^{19} cm^{-3}$ it was still n-type, apparently owing to an extremely small leak across a valve seat of the TMSn tank. Further experiments with tin were temporarily suspended owing to the difficulty in controlling the TMSn flux. The vapor pressure of the compound is so high that even when the tank is held at -45°C, impractically small hydrogen flows through the TMSn tank are required to achieve reasonable doping levels. Tin is an attractive dopant from many respects, including its low toxicity. An examination of the chemical literature indicated that tetraethyltin might be an ideal tin source. The ethyl compound is liquid over a very large range and it should be easy to control the vapor pressure so that there are reasonable hydrogen flows through the tin bubbler. Samples of the material are on order and will be tested in the near future.

Growths were done in an effort to produce an all-OM-VPE-grown metallized shorted junction. The basic idea was to deposit Sb on top of the GaAs:n-type epitaxial layer and then grow the Zn-doped layer on top of this Sb layer. Some structures were processed with the Sb interlayer, but normal diode behavior was observed.

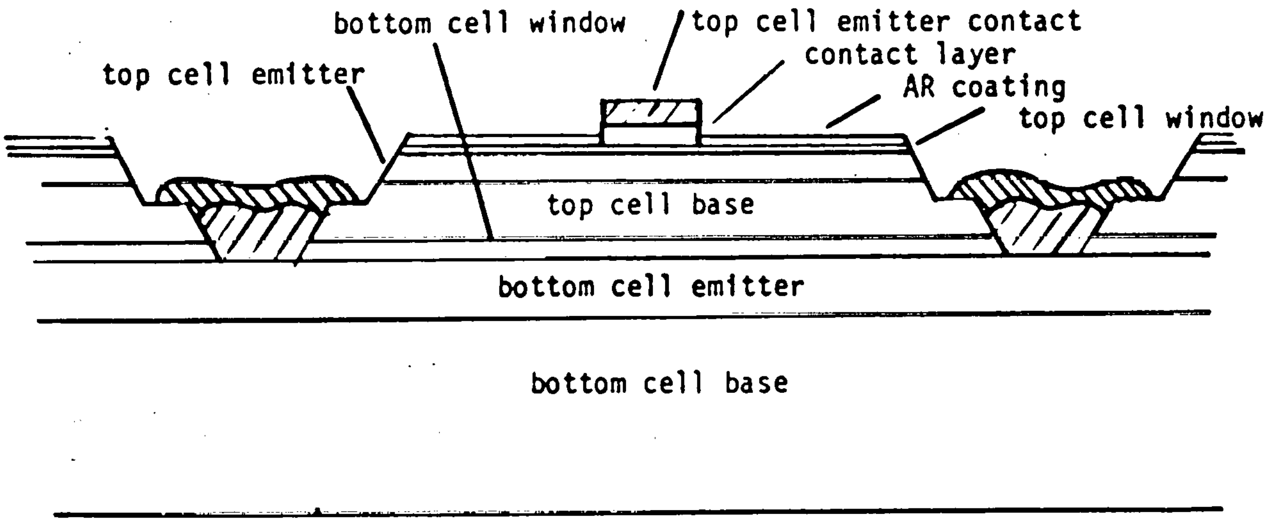
B. Mechanical Interconnects

In addition to the OM-VPE approaches to the interconnect problem described above, an alternate technology was investigated; the metallized stacked cell. The structure of the metallic interconnected cascade cell is best explained with reference to Fig. 5, which shows a cross-section of the device. The salient feature is that a layer of evaporated metal is used to short the top and bottom cell. The groove etching technique relies in part on processing technology developed under Varian's High Voltage Cell Contract.[7]

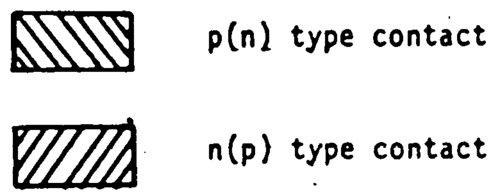
There are several important features of the metallized stacked cell. The ideal interconnect is the OM-VPE-grown tunnel junction, but the metallized interconnect will allow development and optimization of the cascade cell to progress in parallel with tunnel junction development. Since both the top and bottom cells can be probed independently, the metallized stacked cell provides an ideal tool for assessing the contribution of the two individual cells to the overall output. Optimization of each cell can proceed independently of the other. Furthermore, the concept can be used for any appropriate set of III-V high and low bandgap junctions. Device results using this metallized interconnect scheme are discussed under Task 4.

FIGURE 5

SCHEMATIC OF METALLIC INTERCONNECTED CASCADE CELL



NOTE: Dimensions not to scale. Top cell is about 1 micron thick; obscuration at 100 suns is about 10%.



Task 3: AlGaInAs Development

During the last six months' period, there were several significant results related to AlGaInAs development. The range of compositions over which the AlGaInAs could be grown was extended. Work was done to improve the photoluminescence (PL) efficiency and junction efficiency of $Al_{.2}Ga_{.8}As$ epitaxial layers. The techniques developed in this work will be directly applicable to the growth of high-bandgap cells.

A. AlGaInAs Growths

In the previous quarterly report,[2] the growth of AlGaInAs layers over a modest range of compositions was reported. Now the quaternary has been grown over all compositions required for the multijunction cell, including layers with high aluminum content that are suitable for the window layer on the high-bandgap cell. Figures 6-9 summarize the latest results of this work. The substitution of Al for Ga is readily achieved without affecting the lattice constant, an important feature for the growth of the cascade cell.

Difficulties with fogged epitaxial layers were noted for some AlGaInAs growths in the past. Recently, growths have been done at a higher temperature (625°C) with generally better results. A layer of $Al_{.4}Ga_{.4}In_{.2}As$ was grown as a portion of the test structure for the low-bandgap junction (Fig. 1), thereby demonstrating the viability of this quaternary in an actual device structure. Detailed electrical and PL studies are planned for next quarter.

B. AlGaAs Development

During the last six months, some effort was devoted to the study of OM-VPE-grown $Al_{.2}Ga_{.8}As$ layers. Of particular interest is the PL efficiency of the materials and the photoresponse of the junctions in the AlGaAs layers. Experience gained from this work is expected to be directly transferable to work on the AlGaInAs high-bandgap cell.

OM–VPE GROWN $Al_xGa_{1-x-y}In_yAs$

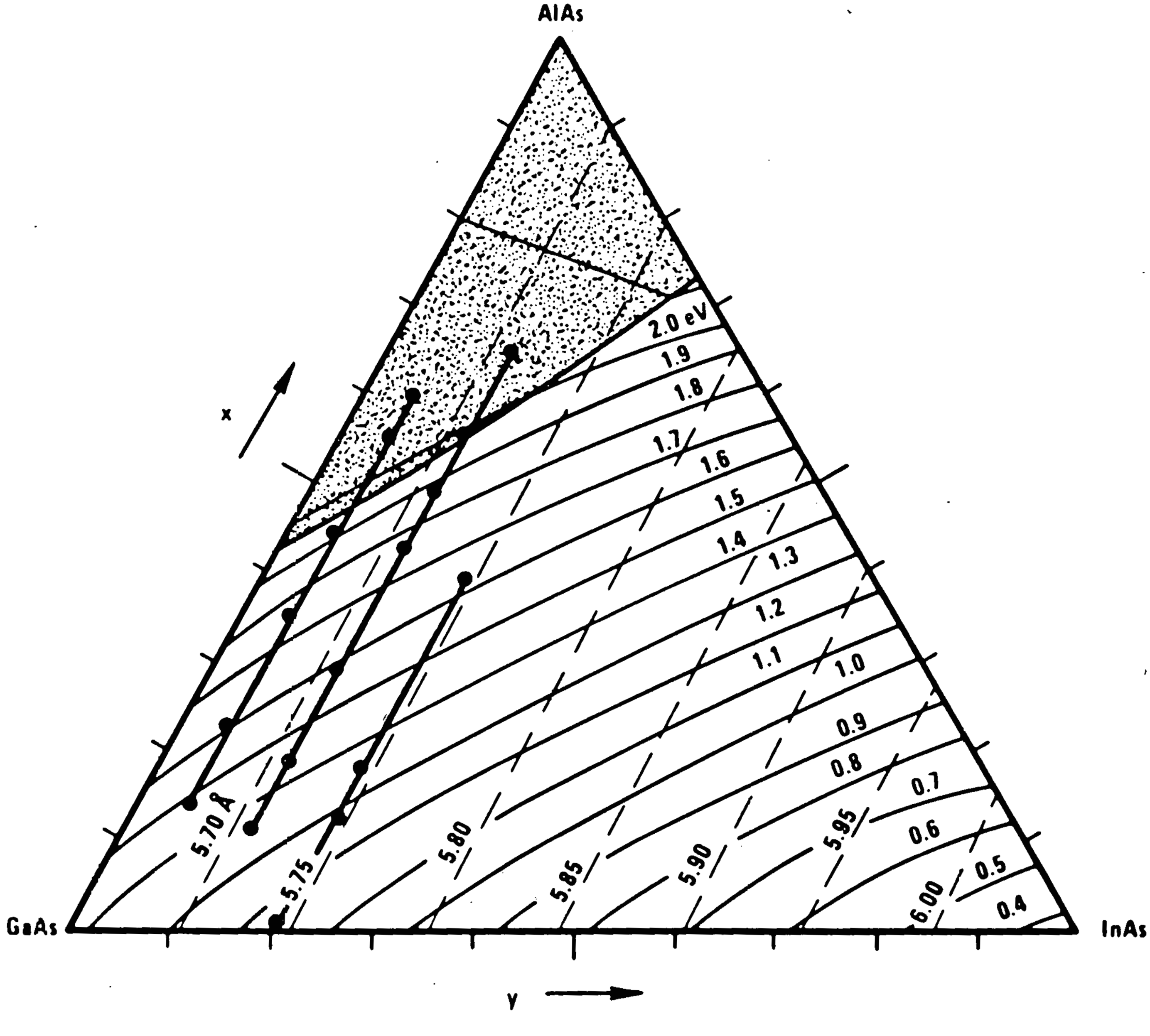
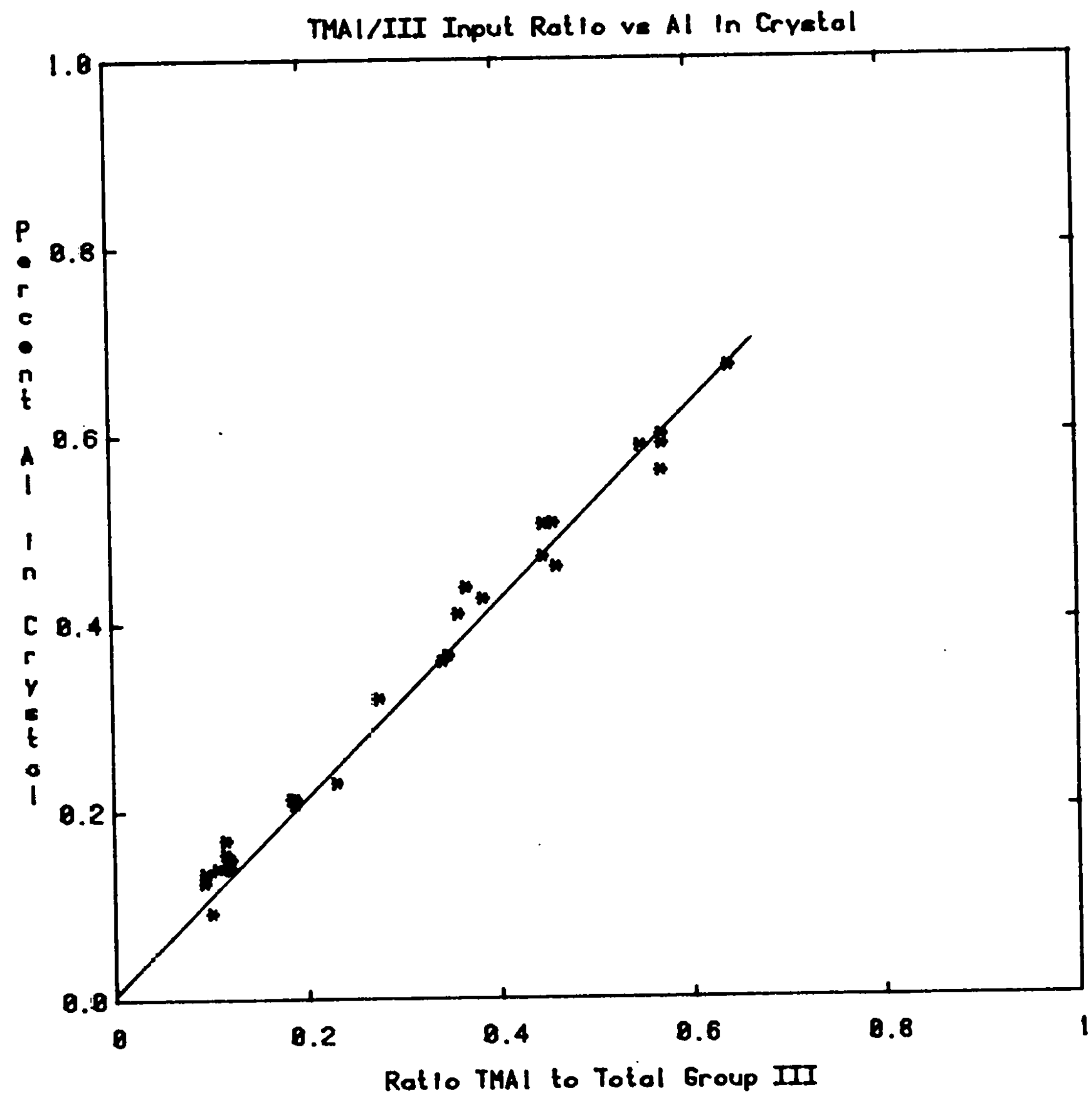


FIGURE 6



TMAl/III Input Ratio vs Al in Crystal
Percent Al in Crystal
1.0
0.8
0.6
0.4
0.2
0.0
0
0.2
0.4
0.6
0.8
1
Ratio TMAl to Total Group III

FIGURE 7

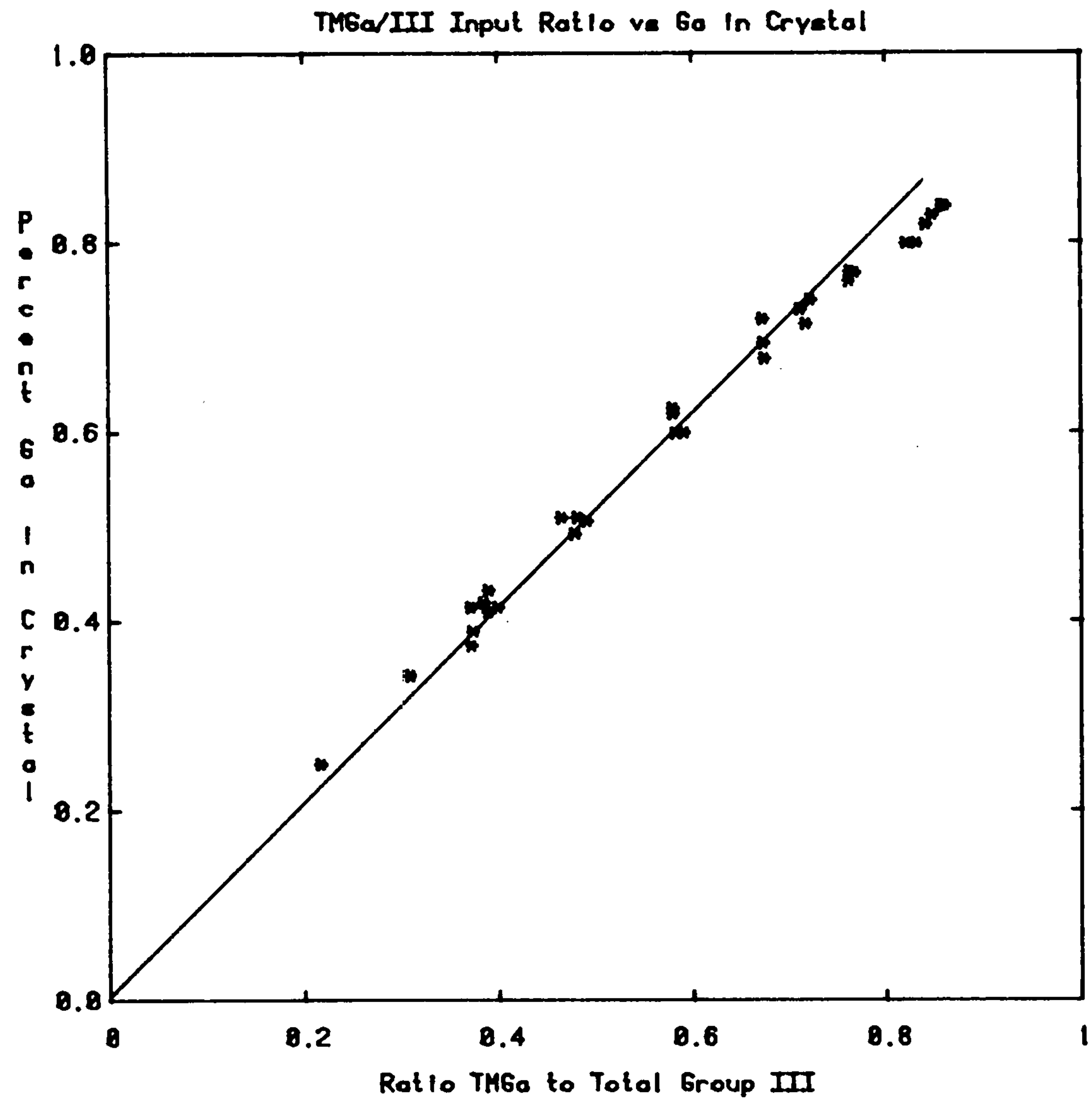

TMGa/III Input Ratio vs Ga in Crystal
Percent Ga in Crystal
1.0
0.8
0.6
0.4
0.2
0.0
0
0.2
0.4
0.6
0.8
1
Ratio TMGa to Total Group III

FIGURE 8

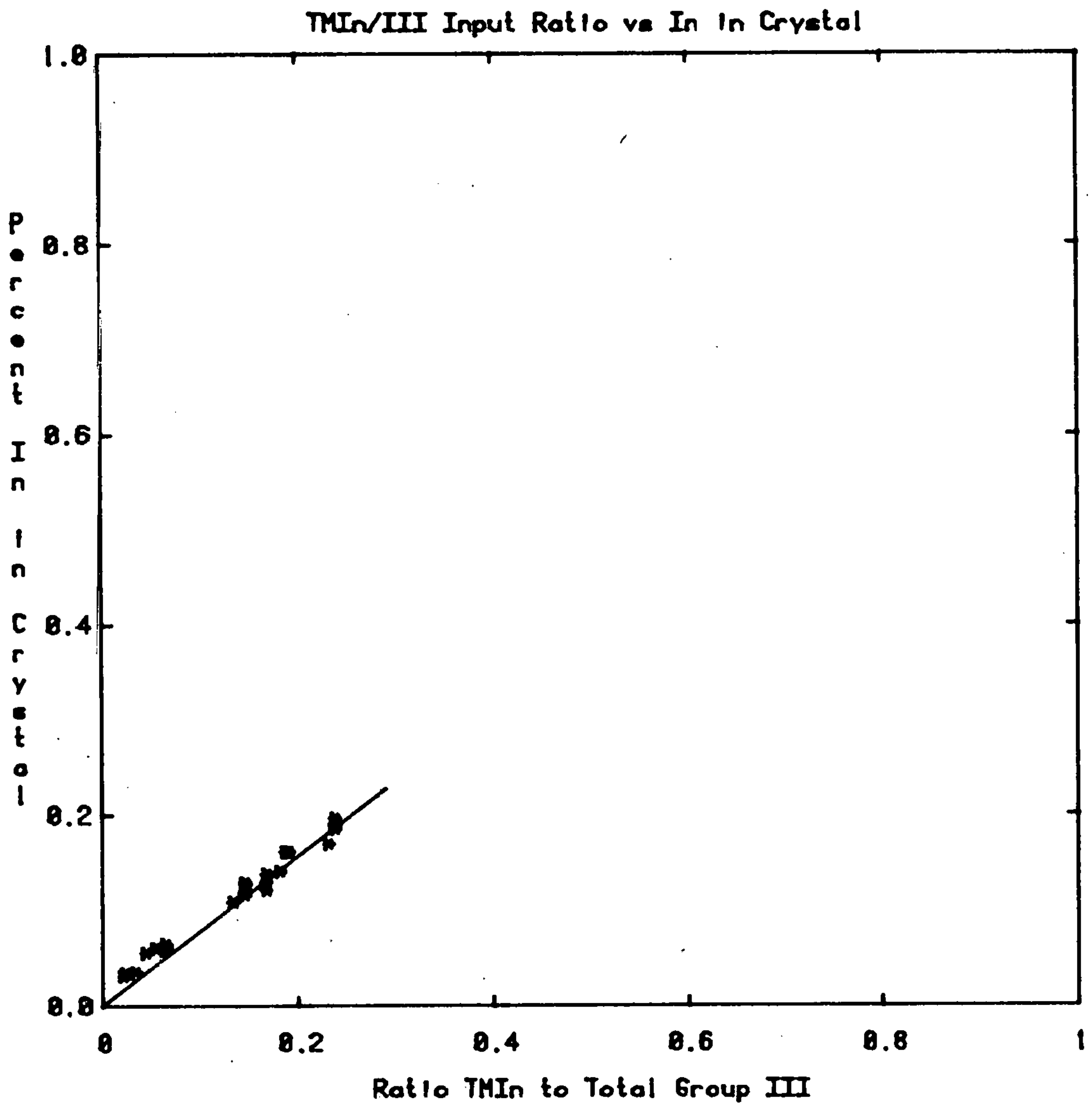

TMIn/III Input Ratio vs In in Crystal
Percent In in Crystal
Ratio TMIn to Total Group III
1.0
0.8
0.6
0.4
0.2
0.0
0
0.2
0.4
0.6
0.8
1

FIGURE 9

Recently, Stringfellow[8] described the use of graphite baffles to getter impurities and thereby improve the PL efficiency of OM-VPE-grown AlGaAs layers. We have developed a similar technique that has resulted in good PL efficiency from $Al_{.2}Ga_{.8}As$ epitaxial layers. Figure 10 shows a comparison of the PL response from a bulk GaAs sample and an OM-VPE-grown $Al_{.2}Ga_{.8}As$:Zn sample. Although PL efficiencies are ~1/4 that of the bulk sample (uncorrected for doping levels), it is a vast improvement over previous results.

The photoresponse of the $Al_{.2}Ga_{.8}As$ junctions has also improved. In the past there was essentially no photoresponse from OM-VPE-grown AlGaAs junctions. However, the in-line gettering of impurities has allowed the growth of good-quality junctions, as illustrated in Fig. 11. This result is highly significant, since it is the first OM-VPE-grown high-bandgap (1.65 eV) cell with good photoresponse. Furthermore, this junction was grown early in the study and refinements in the process are expected to result in significantly improved efficiencies. This advantage paves the way for the demonstration of an all-OM-VPE-grown cascade cell using the metallized, stacked cell interconnect (see Task 4).

Task 4: Cascade Cell Fabrication

Completion of this task will represent successful integration of Tasks 1, 2 and 3. Sufficient progress has been made that an all-OM-VPE-grown cascade cell can be fabricated. The key advances as discussed earlier are the development of the metallized stacked cell interconnect and the substantially improved photoresponse of the $Al_{.2}Ga_{.8}As$ junctions.

The idea is to demonstrate the all-OM-VPE-grown cascade cell with materials that are well understood, then transfer the technology to the prime materials system of interest. The bottom cell is based on Varian's highly successful GaAs solar cell,[3] where as the top junction is a 1.65-eV $Al_{.2}Ga_{.8}As$ cell. Although these two bandgaps are far from optimized, fabrication and testing of this cascade cell is expected to provide valuable experience.

COMPARISON OF PHOTOLUMINESENCE INTENSITY OF OM-VPE AlGaAs AND BULK aAs

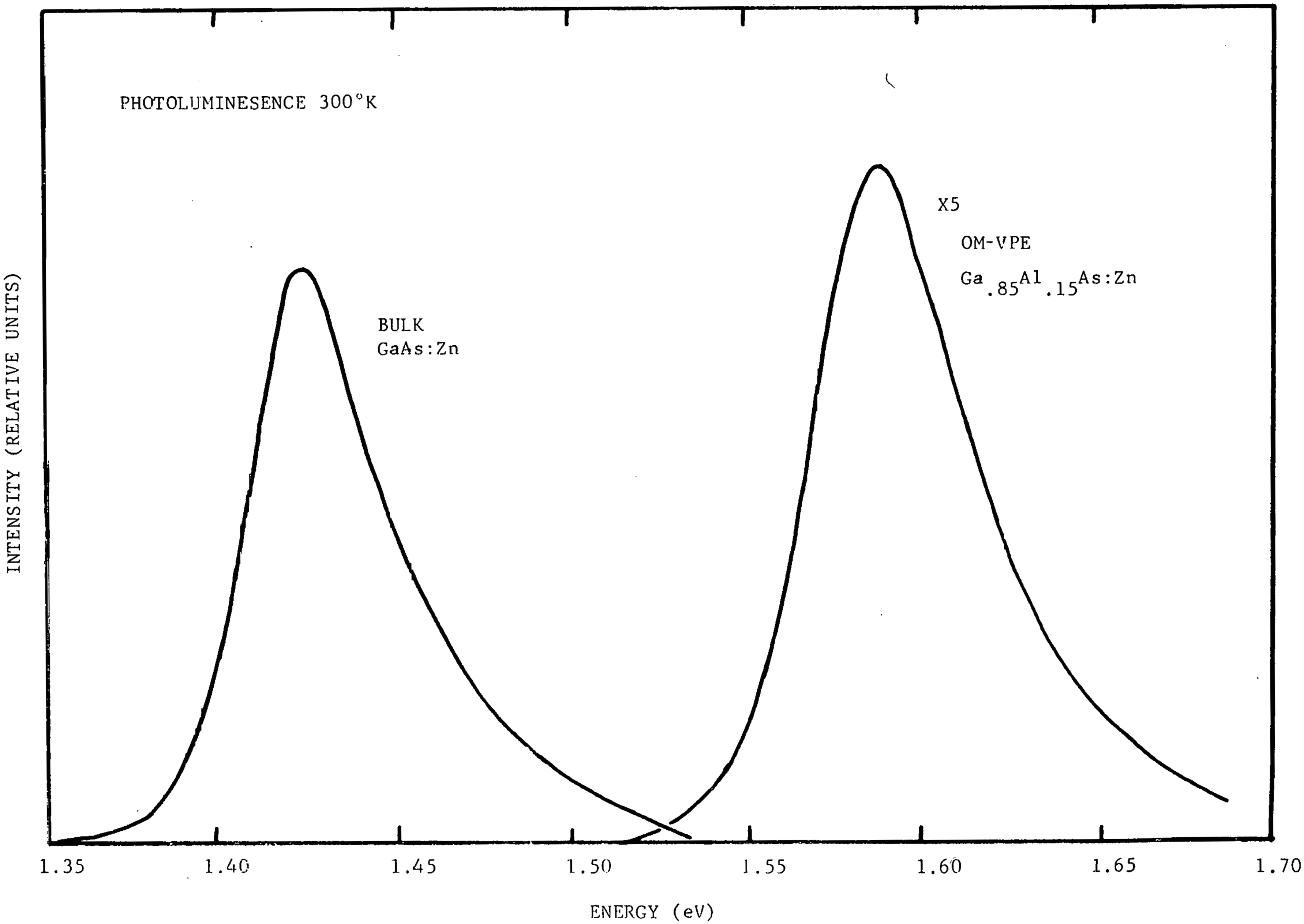
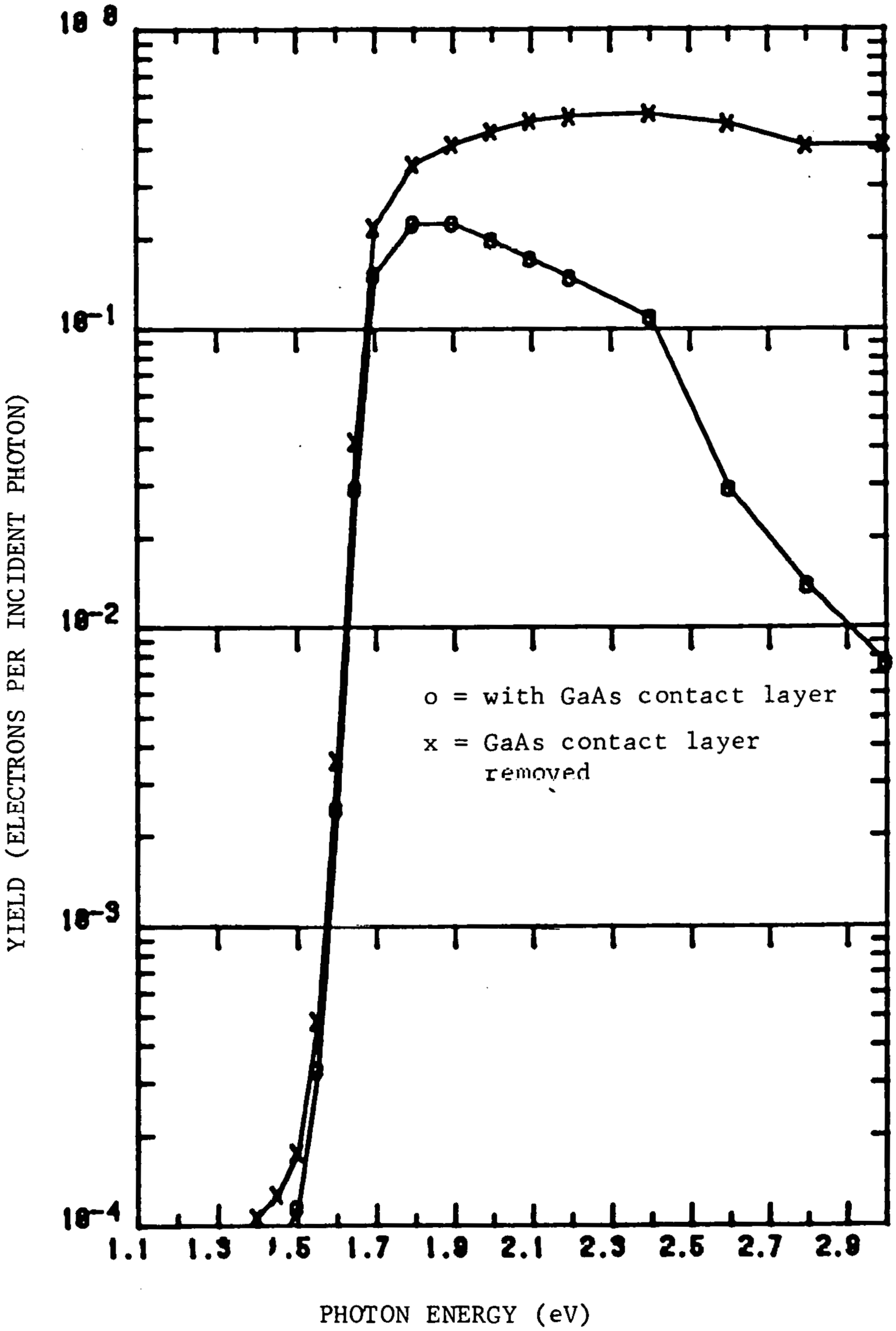


FIGURE 10

FIGURE 11

PHOTORESPONSE OF $Al_{.2}Ga_{.8}As$ CELL



Several two-junction structures were grown and processed. Initial difficulties were processing-related and changes were made in the epitaxial layers to circumvent these problems. Results have been very encouraging and the latest structure, currently in process, is expected to show the desired voltage addition.

Work during the next quarter will center on optimizing the AlGaAs/GaAs cascade cell process, including studies of each of the junctions in the structure. Once a viable high-gap cell is demonstrated in AlGaInAs, a metallized stacked cell can be demonstrated in this materials system.

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