VACUUM MOCVD FABRICATION OF HIGH EFFICIENCY CELLS FOR MULTIJUNCTION APPLICATIONS*

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Vacuum metal-organic-chemical-vapor-deposition (MOCVD) is a new fabrication process with improved safety and easier scalability due to its metal rather than glass construction and its uniform multiport gas injection system. It uses source materials more efficiently than other methods because the vacuum molecular flow conditions allow the high sticking coefficient reactants to reach the substrates as undeflected molecular beams and the hot chamber walls cause the low sticking coefficient reactants to bounce off the walls and interact with the substrates many times. This high source utilization reduces the materials costs per device and substantially decreases the amounts of toxic materials that must be handled as process effluents. The molecular beams allow precise growth control. With improved source purifications, vacuum MOCVD has provided p GaAs layers with 10-μ minority carrier diffusion lengths and GaAs and GaAsSb solar cells with 20% AM0 efficiencies at 59X and 99X sunlight concentration ratios. Mechanical stacking has been identified as the quickest, most direct and logical path to stacked multiple-junction solar cells that perform better than the best single-junction devices. The mechanical stack is configured for immediate use in solar arrays and allows interconnections that improve the system end-of-life performance in space. A GaAsP cell of 13% AM0 efficiency has been fabricated onto a transparent GaP substrate (GaAsP/GaP). Mechanically stacking this GaAsP/GaP on current technology silicon cells would give a combined 20% AM0 performance. Practical efficiency levels of fully developed systems should be 27% AM0 for GaAsP/GaP on silicon and approaching 30% AM0 for GaAsP/GaP on a direct band gap bottom cell. Incorporating these devices in light concentrator systems offers the highest efficiencies, the best tolerance of nonideal device behavior, and the most protection against damaging radiation.

INTRODUCTION

Vacuum MOCVD is a new fabrication process that has been under development at Chevron Research for the past several years (ref. 1) to produce high efficiency solar cells. A novel and beneficial feature of the vacuum configuration is that gas transport is by molecular flow, while in higher pressure, conventional MOCVD it is by laminar flow. The vacuum configuration incorporates some of the best features of molecular beam epitaxy (MBE). It produces high quality layers and solar cell junctions equivalent to the best obtained by other methods. It is well suited to the formation of solar cells on a transparent substrate which can readily be stacked mechanically onto another cell to form multiple-junction devices. Multiple junctions offer the potential for significantly improved device performance (ref. 2). Mechanical stacking circumvents many of the problems encountered in other multiple-junction configurations and it provides cell interconnections that improve the end-of-life efficiencies limited by different junction degradation rates in space.

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When the series resistance and device temperature can be kept sufficiently low, concentrated light systems offer the best overall performance characteristics.

VACUUM MOCVD

A simplified schematic of the vacuum MOCVD system is shown in figure 1. The operating pressure of the reactor is in the 1 millitorr range where convective heat loss is negligible. In conventional higher pressure systems, such convective losses are large enough that multikilowatt, radiant, or RF induction heaters are required to maintain the 600-700°C reaction temperatures. For heating energy transmission, these systems use glass- or quartz-walled chambers. In contrast, the required temperatures in the present vacuum system are produced by a 600-watt resistance heater. The whole figure 1 system, including the heater, is enclosed by a stainless steel outer chamber (not shown) which remains at room temperature. This improves the safety in handling the toxic and pyrophoric gas sources because there are no strong temperature stresses on the outer walls and because the metal does not shatter like glass. In addition, any small gas leaks are into, rather than out of, the vacuum enclosure. Since the main structural element is steel, the system can be scaled up in size more easily than glass-based systems. The multiple gas injection ports shown in figure 1 maintain the growth uniformity during such scaling.

Figure 1 illustrates the epitaxial growth of GaAs onto a GaAs substrate. The source gases of arsine (AsH_3) and triethylgallium (TEG) are fed in from the side and bottom, respectively, of the inner graphite reactor chamber, which has hot walls. This configuration combines some of the best features of MBE and traditional CVD while avoiding some of their serious problems. The expensive and comparatively rare TEG is used efficiently. In the molecular flow vacuum, the TEG molecular beam delivers Ga directly to the substrate without deflection and with a high sticking coefficient (ref. 3) that is dependent on the AsH_3 overpressure (ref. 4). The sticking coefficient is less than one since some GaAs forms on the bottom wall of the graphite chamber. Essentially all the TEG reacts in the chamber with none detected at the exit port with a residual gas analyzer (RGA). This indicates a Ga utilization efficiency of the order of 50% or greater for large-scale systems with planar geometry where multiple TEG injection nozzles provide growth uniformity. The AsH_3 distributes uniformly throughout the reaction chamber due to its low sticking coefficient (estimated 0.01 value) and its multiple bounces off the hot chamber walls. This provides many opportunities for the AsH_3 to react on the substrate surface. An AsH_3 overpressure is required for good epitaxy (ref. 3), and the AsH_3/TEG flow ratio of 6:1 used in this system indicates an AsH_3 utilization of the order of 15%. Upstream decomposition of the AsH_3 in a thermal cracker (shown in fig. 1) gives more efficient growth with a reduced AsH_3/TEG flow ratio of 3:1 and a 30% estimated AsH_3 utilization. A strong AsH_3 signal is detected by the exit port RGA under all these conditions.

The gas utilization is much lower in the conventional, higher pressure, laminar flow MOCVD systems. Only those molecules in the boundary layer next to the substrate contribute to the epitaxial growth. Most of the gas is swept past the substrates without touching them. This gives Ga utilization of the order of a tenth or less. These systems are cold walled and require much higher AsH_3 over pressures with arsenic-to-gallium flow ratios typically in the 20-100 range (ref. 5). Such wastes increase the materials cost per device by at least a factor of two. The problems of safe effluent management are multiplied by the orders of magnitude higher volumes of toxic AsH_3 released through the exit port of higher pressure systems. In MBE machines using AsH_3 (ref. 4), most of this gas is lost since it has essentially a single chance to strike the substrate. MBE growth uniformity is

difficult to achieve with a single Ga injector nozzle (ref. 3). The multiple molecular Ga beams in the present vacuum MOCVD system provide for uniformity along with the precise growth control characteristics of MBE.

MATERIALS AND DEVICES

A continuing problem of MOCVD is that source material quality is only beginning to be improved to the level of older techniques like liquid phase epitaxy (LPE). However, recent advances in moisture removal from AsH_3 (ref. 6) and purification of the p dopant source (ref. 7) have provided layer growths of high quality. Figure 2 shows the quantum yield spectra measured on a special n^+ on p GaAs sample fabricated by vacuum MOCVD. The n^+ layer was degenerately doped so that its contribution to the quantum yield was negligible due to Auger recombination (ref. 8 and 9). The resulting curve fits show that the electron diffusion length (L_n) in the p layer is 10 μ. This is equivalent to the best values achieved by other growth techniques including LPE.

Figure 3 shows the I-V properties of two p on n solar cells grown by vacuum MOCVD with 20% AM0 efficiencies at sunlight concentration ratios of 59X and 99X. The ternary GaAsSb cell was formed with molecular beams (see fig. 1) of both TEG and triethylantimony using a GaAs substrate and a graded Sb composition transition layer. The external quantum yields of these devices are shown in figure 4. Their peak values are 90% and 95% and flat, indicative of long diffusion lengths and low surface recombination velocities. The GaAsSb band gap is 1.35 eV. Both cells had surface passivation by a several hundred-angstrom thick layer of AlGaAs or AlGaAsSb formed by switching on a triisobutylaluminum molecular beam at the end of their growths. Both cells also had two-layer antireflection coating applied. This performance is equivalent to the state-of-the-art results reported for other fabrication techniques. All the solar cells reported in this paper have 0.0386 cm^2 active areas, and all the efficiencies are active area values.

We have previously reported the I-V properties and quantum yield (ref. 10) for a vacuum MOCVD p on n GaAsP cell with 15% AM0 efficiency at a 112X concentration ratio. (The corresponding AM1.5 efficiency was 17% at 133X concentration.) This cell had a band gap of 1.6 eV and was grown on top of a GaAsSb device on a GaAs wafer. It was grown with PH_3 gas injected into the reaction chamber through a port similar to that used for AsH_3 injection. This illustrates the variable band gap fabrication capability of vacuum MOCVD for ternary III-V solar cells.

MECHANICAL STACK

The 20% AM0 performance is beginning to approach the practical limits of efficiencies that can be readily achieved with single-junction solar cells (ref. 11). However, stacking two different band gap cells one on top of the other offers the potential for substantially higher performance levels (ref. 2). In particular, stacking a GaAsP cell onto a current technology Si cell is promising. Figure 5 shows the 13% AM0 efficiency with 64X concentration achieved in a preliminary experiment with a GaAsP cell grown onto a transparent GaP substrate. The calculations show (ref. 12) that mechanically laying this device on top of a silicon cell would give a combined AM0 conversion efficiency of slightly over 20% with a 250-μ thick GaP wafer and appropriate antireflection coatings. A fully developed GaAsP/GaP top cell should alone approach an efficiency of about 20%. Mechanically stacking such a cell on a silicon device should then provide practical performance levels in the 27% AM0 range (ref. 12). Much of the ground work for GaAsP on GaP has already been laid by the development of light-emitting diodes which use the same

materials layers and p-n junction structure. Replacing the bottom silicon cell with a fully developed, direct band gap material with higher quantum yield (for example, GaAsSb--see figure 4) should provide mechanical stack performance approaching the 30% AMO level.

The mechanical stack circumvents many of the problems that are currently impeding the progress of other stacked, multijunction designs. It is a four-terminal device that eliminates the need for the shorting junction that has proved difficult to achieve in monolithic layered devices. It simplifies the problems of transition layers. With a GaAsP cell monolithically stacked onto a GaAsSb cell as described in reference 10, a several-micron thick transition layer is required between the two junctions to attain high performance in the top GaAsP; but this thick layer absorbs photons and limits the efficiency of the bottom cell (to 4% in reference 10). Addition of Al to the transition layer reduces the absorption, but the performance of the top GaAsP junction is substantially reduced because of problems related to the Al layer. These basic materials problems are all solvable given enough time and effort. However, the quickest, most direct and logical path to high performance multijunctions ready to use in arrays is the mechanical stack.

The monolithic, two-junction stack of reference 10 is a three-terminal device that circumvents shorting junction problems by using a p-n-p configuration. Before it could be used in an array, the complimentary n-p-n two-junction device would have to be developed. All the involved junctions would need to be current matched for series connections.

The four-terminal versatility of mechanical stacks allows the devices to be connected so that end-of-life system performance is improved. With different junctions exposed to the space radiation environment, each junction would be expected to degrade at a different rate. If stacked cells were designed for series connection with currents matched at the beginning of life, their currents would be mismatched at end of life with performance loss greater than the efficiency loss of each individual junction. Voltage matching provides a more robust space design since device voltages only vary logarithmically with current changes. Figure 6 shows a 4 by 2 module wiring diagram for voltage matching of top and bottom cells whose output voltages differ by a factor of two. This can be achieved in GaAsP and silicon by selecting the correct GaAsP band gap. For the eight-element configuration, four of the bottom cells and two of the top cells are connected in series to provide the voltage match. For the other operating voltage ratios, other series-parallel connections schemes (e.g., 4 by 3, 7 by 5, etc.) can be used to achieve voltage matching.

CONCENTRATORS

Since the short circuit current of solar cells increases linearly with light intensity, their efficiency would remain constant under concentrated light if their open circuit voltage and fill factor remained constant. However, the voltage increases logarithmically with this current rise and the fill factor also increases (ref. 13). The net result is an increase in device performance with concentration as long as series resistance and device temperature can be kept sufficiently low. For 100X concentration and 5% grid contact coverage, grid contact resistances below about 10^{-4} ohm-cm^2 are required to prevent loss of fill factor. Values in this range were achieved in the figure 3 p on n devices using a silver alloy p layer contact, 500-μ grid line spacing, and 15-μ wide grids. The silver, containing 4.5% manganese by weight (Cominco), was electron beam deposited 1500 angstoms thick onto the p layer. This was annealed in forming gas for one minute at 450°C and then

electroplated with 2-3 μ of silver. Ohmic contact was assured as long as the p layer doping level was above 1 (10^{18}) cm^{-3}. The diffusion length was not seriously decreased by Auger recombination (ref. 8 and 9), as long as the p doping was less than 2 (10^{18}) cm^{-3}. Curtice (ref. 11) has calculated the trade-offs among device temperature, efficiency, and concentration ratio for GaAs cells used in space. He found the 50-100X range as near optimal. This range spans the figure 3 conditions where the 20% devices were measured.

An additional advantage of concentrators is that shunt leakage paths can become saturated at the higher current levels encountered. This means that devices can exhibit near ideal performance with high efficiency at concentration even though their characteristics would be dominated by efficiency lowering leakage at unconcentrated light levels. Thus, the concentrator applications are more tolerant of nonideal device behavior. A final advantage of concentrators is the extra protection they afford the devices. Most concentrator designs for space have the devices completely surrounded by metal structures (ref. 14). This provides shielding from damaging radiation like cosmic rays or from high intensity optical radiation not directly aligned with the optical axis of the concentrator.

CONCLUSIONS

Vacuum MOCVD is a novel fabrication method being developed at Chevron to produce high quality materials for high efficiency solar cells. It combines the precise control of MBE with the high throughput of CVD. It uses the source materials more efficiently than alternate methods and reduces the materials costs per device by at least a factor of two. It decreases the volume of toxic effluents that must be handled by an order of magnitude and reduces the dangers of toxic gas escape by replacing fragile glass outer walls of higher pressure MOCVD with steel. It is more easily scalable to higher volume production because the steel structural parts can be increased in size in a more straightforward manner than glass, while the multiple injection ports maintain uniformity. Recent improvement in source quality have given materials with properties equivalent to the best produced by other fabrication techniques including LPE. These properties include p material with a 10-μ minority carrier diffusion length. Solar cell devices have been produced with 20% AM0 efficiencies at concentration ratios of 59X and 99X using GaAs and GaAsSb p on n junctions.

A mechanical stack has been identified as the most rapid, direct, and logical path to stacked, multijunction devices that can be immediately incorporated into actual arrays and that have performance levels exceeding the best single-junction performance. A preliminary experiment has given a GaAsP device of 13% AM0 efficiency on a transparent GaP substrate. Mechanically stacking this device on present technology silicon cells would provide 20% AM0 efficiency. Full development of this configuration should give practical performance levels around 27% AM0 with silicon and approaching 30% AM0 with a direct band gap device for the bottom junction. Module wiring schemes to produce voltage matching are easily achieved with mechanical stacks and these schemes give multijunction systems with superior end-of-life performance in space. Concentrator systems give the highest device performance, are the most tolerant of nonideal device behavior, and provide extra protection against radiation damage as long as series resistance is sufficiently low. Silver-manganese metalizations have given low enough contact resistance for 20% efficient (AM0), concentrated light performance at up to 100X.

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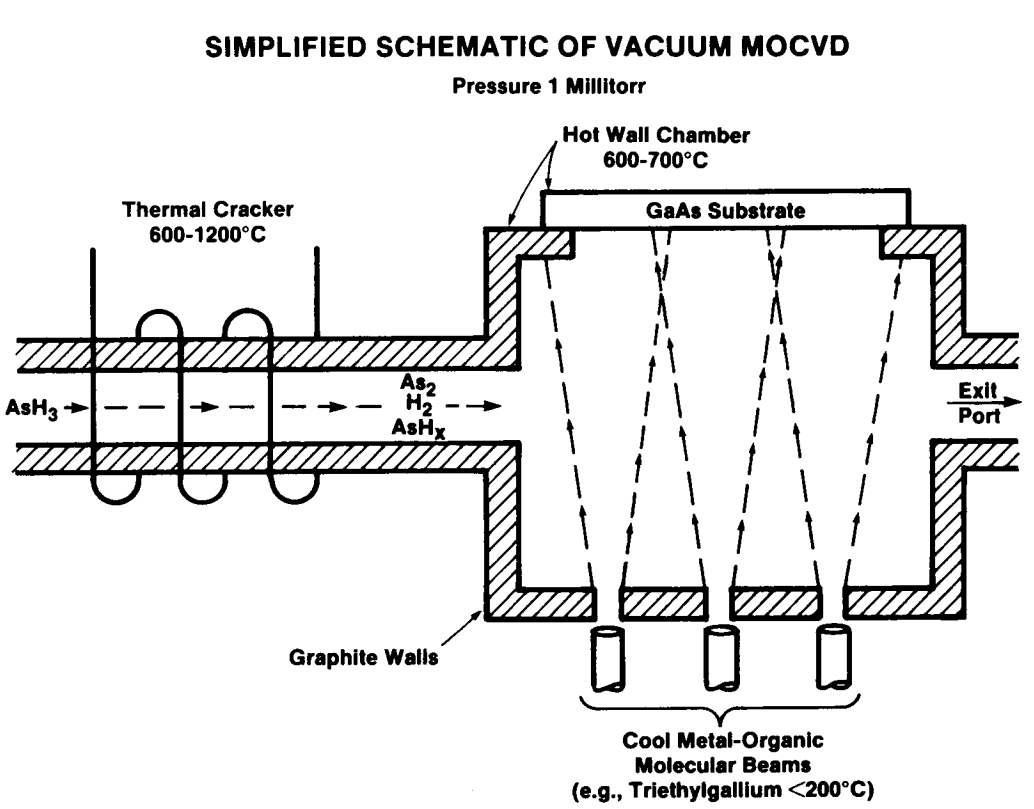

Figure 1. Schematic diagram of the vacuum MOCVD system showing the growth of GaAs epitaxial layers on a GaAs substrate.

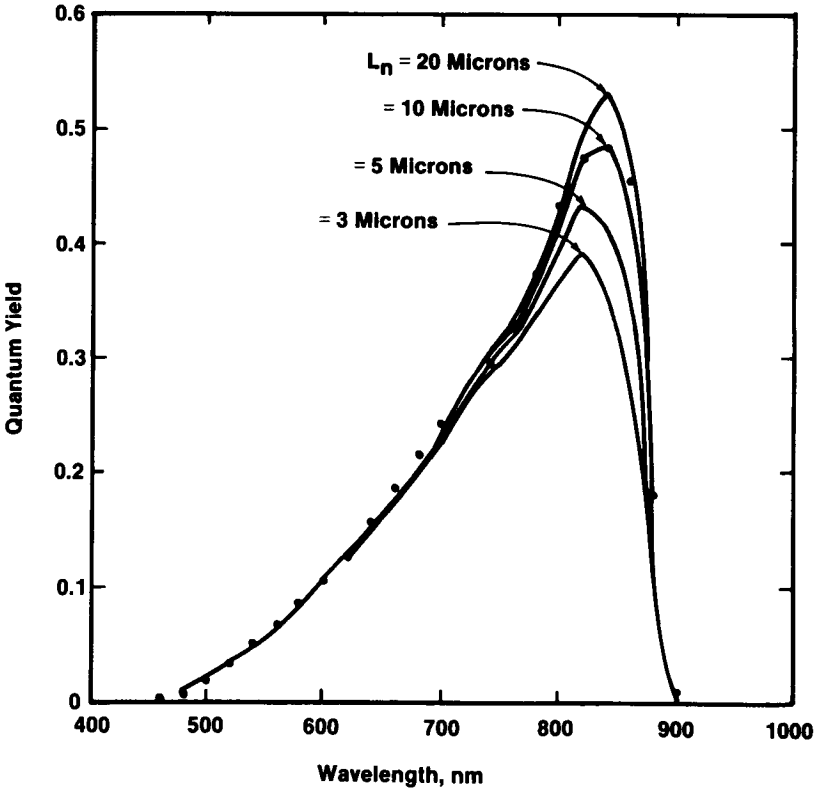

Figure 2. Theoretical curve fit of measured quantum yield data points indicating a 10-μ diffusion length in the p layer of a n^+-p junction.

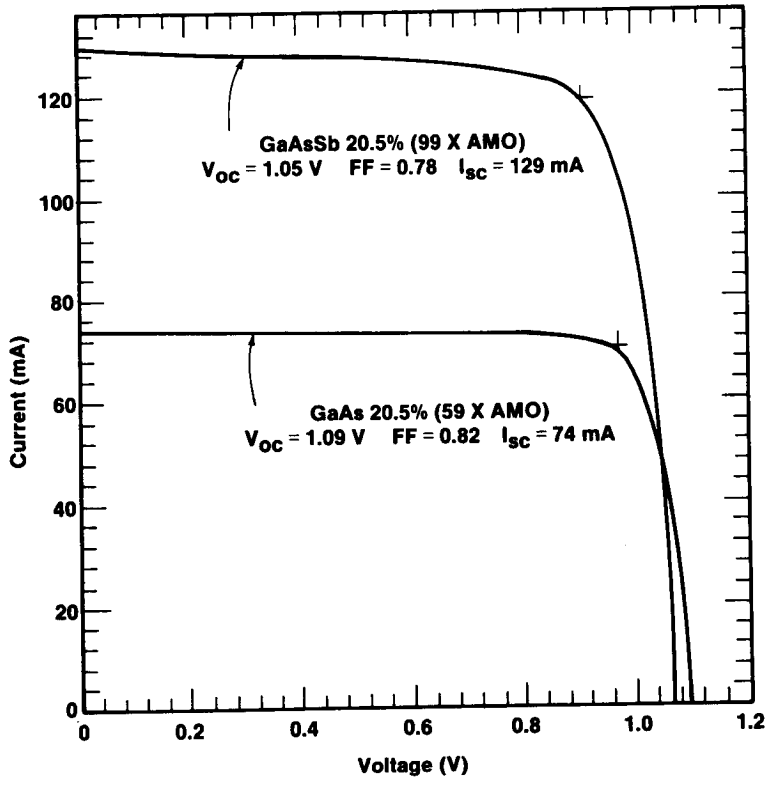

Figure 3. The flash simulator measurements of the I-V properties of GaAs and GaAsSb solar cells with 20% AMO efficiencies.

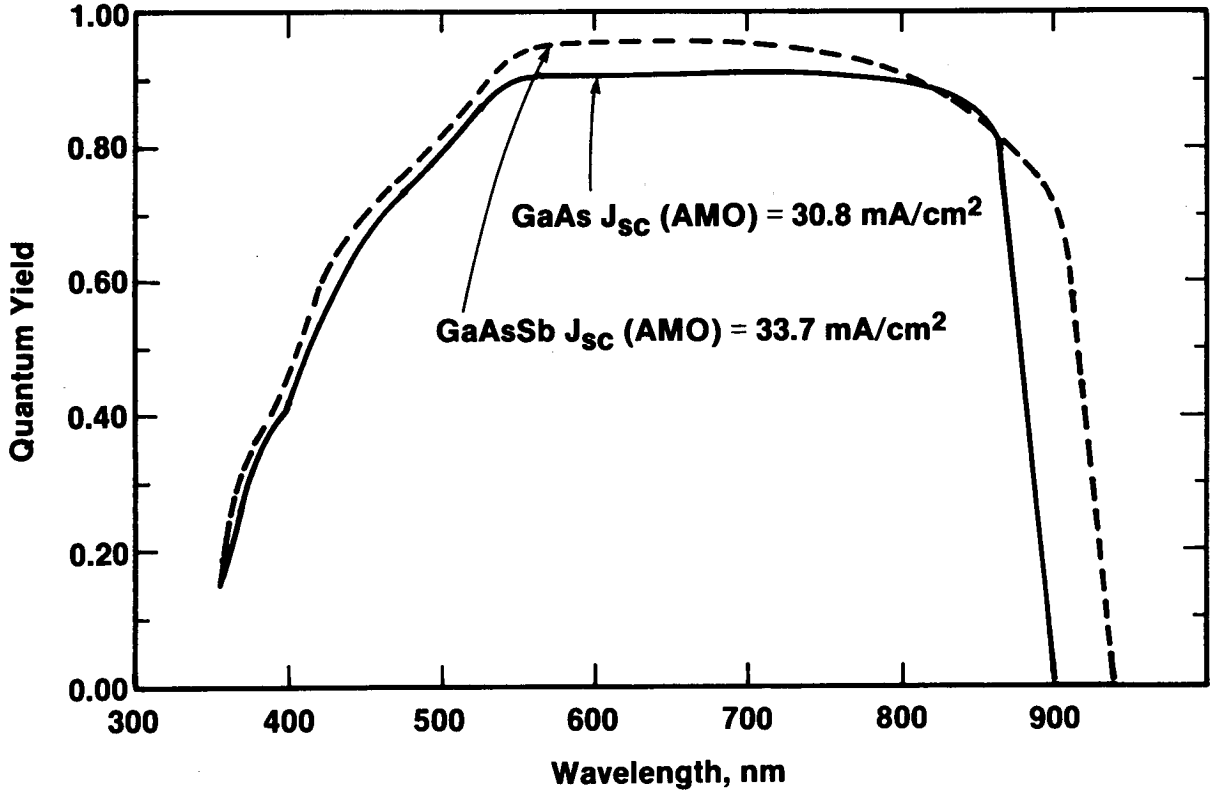

Figure 4. The external quantum yields measured on the two cells whose I-V properties are shown in figure 3.

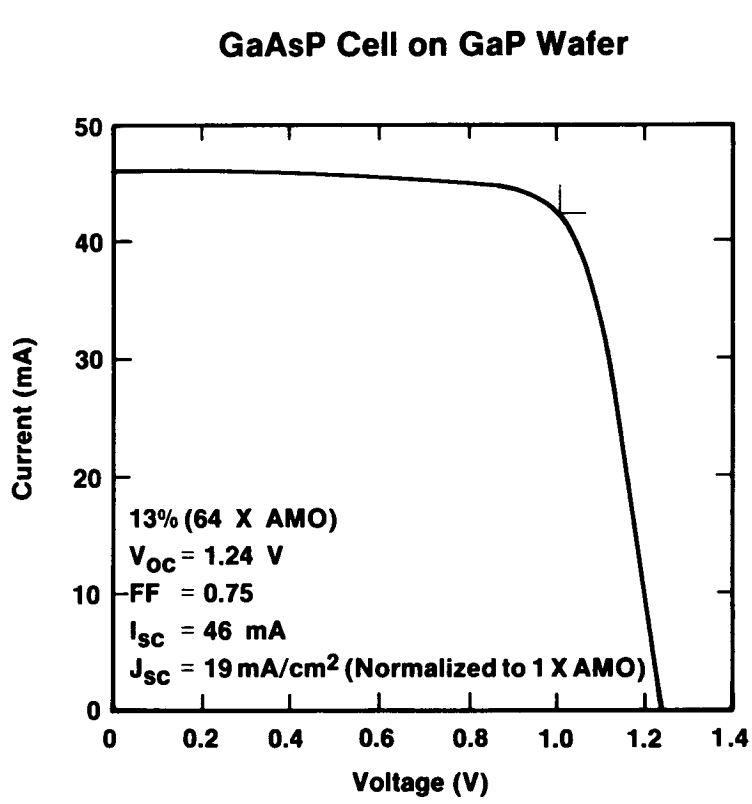

Figure 5. The flash simulator measurement of the I-V properties of the GaAsP solar cell formed on a transparent GaP wafer.

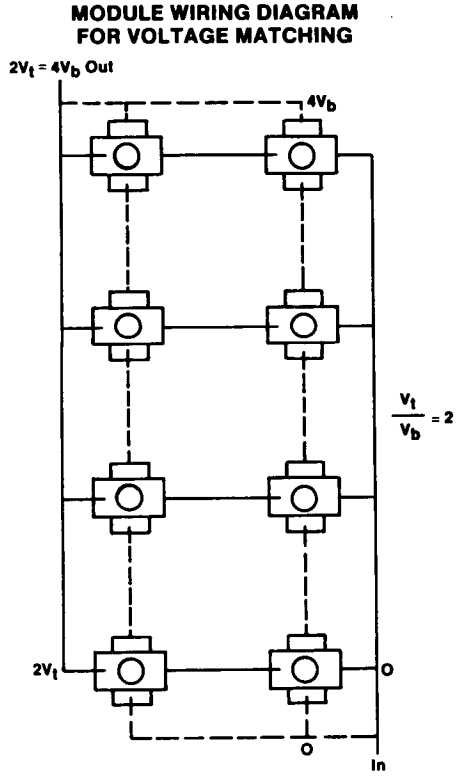

Figure 6. The 4 by 2 module wiring diagram for voltage matching stacked solar cells with a 2:1 voltage output ratio and four terminals available for interconnections.