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QUARTERLY

TECHNICAL PROGRESS REPORT NO. 2

MASTER

DEVELOPMENT OF HIGH EFFICIENCY CASCADE SOLAR CELLS

December 31, 1979

Contract XM-9-8136-1 under DOE EG-77-C-01-4042

RTI Project 41U-1846

Solar Energy Research Institute

Golden, Colorado

RESEARCH TRIANGLE PARK, NORTH CAROLINA 27709

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Quarterly

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Introduction

This report summarizes the work conducted under the present contract during the quarterly period 1 October to 31 December 1979.

Research has continued in the development of selected ternary and quaternary III-V materials that are potential candidates for cascade solar cell applications. In addition, various simple and multi-junction cascade solar cell components have been fabricated and evaluated in a continuing study of several different solar cell designs (materials combinations).

During the present reporting period, work has concentrated on the following major areas:

GaAlAs/GaAs Cell Development

AlGaAsSb/GaAsSb Materials Development

GaInP Materials Development via VPE

Inverted Structure Development

MO/CVD Growth System Work at NCSU

Progress in each of these areas is summarized below.

GaAlAs/GaAs Cell Development

The GaAlAs/GaAs materials system remains the only system in which a cascade solar cell has been demonstrated. This materials system, which is theoretically capable of ≈25 percent efficiency under 1 sun illumination, is the most advanced system from a developmental standpoint and has been singled out for further development under Air Force Contract F 33615-78-C-2077.

Three different structures have been considered for a two-junction AlGaAs/GaAs cascade cell as depicted in Figure 1.

Structure (a) has been successfully fabricated, but its main disadvantages are the large number of layers required and the fact that the metallurgical junction coincides with the electrical junction in the top cell; this makes it difficult to reproducibly obtain a good quality top cell with

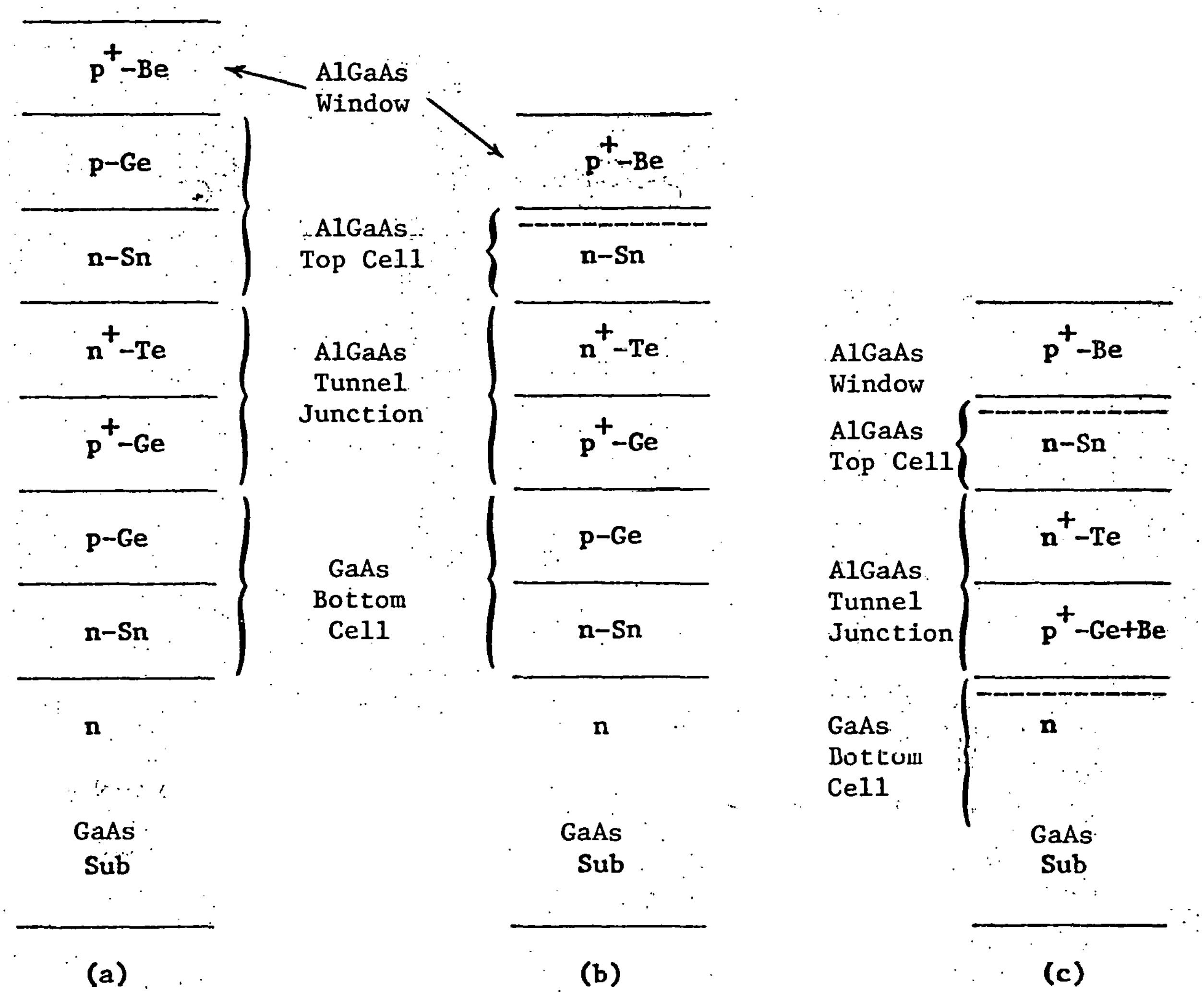

Figure 1. AlGaAs/GaAs Cascade Cell Configurations

an adequate V_{oc}. Spectral response data obtained on one of these structures is shown in Figure 2. This particular sample had an upper cell bandgap of approximately 1.8 eV and was capped by a window layer without an antireflection coating. This spectral response measurement was made using a chopped and filtered light source over the 1.37 to 2.07 eV range in conjunction with d.c. light sources of 1.46 eV and 1.91 eV used alternately to turn on the bottom and top cells, respectively. The two broad peaks in Figure 2 correspond approximately to the AlGaAs and GaAs cell bandgaps.

Structure (b) has also been built with both junctions optically active; however, $V_{oc} \approx 1.5V$ was measured for the overall structure. This is much too low for satisfactory operation. The V_{oc} of the top cell was about 0.7 V, which is also well below the desired value. This problem is believed to stem from lattice defects introduced into the top cell by the underlying tunnel junction.

Because of its simplicity, structure (c) is the most attractive version of the cascade cell and considerable efforts will be focused on this structure. Both top and bottom diffused junction cells have been demonstrated but attempts to grow the overall structure have thus far not been successful due to difficulties with the top cell when fabricated on the bottom cell + connecting junction.

1. Top Cell Development

The top cell junction has been fabricated (structure c) via the diffusion of Be. Be has been chosen as a dopant because of its low vapor pressure compared to that of Zn or Mg. Be diffusion into the n-$Al_{0.35}Ga_{0.65}As$ layer during the growth of the p^+-$Al_{0.9}Ga_{0.1}As$ window layer gives reproducible results for junctions grown directly on GaAs substrates. However, when such a junction is grown on the bottom cell and the tunnel junction (the whole structure), results are usually unpredictable and the top cell is frequently shorted.

The diffusion of Be is typically characterized by analomous behavior and at times seems not to follow Fick's law in that the diffusion coefficient of Be in the solid may be dependent on the concentration of Be in the melt. This concentration (a few µg of Be per gm of Ga) is very hard to control reproducibly especially with a very reactive material such as Be. Thus, in most of the cases, Be diffuses for distances larger than the thickness of the n-AlGaAs layer and the top cell is shorted. We intend to try Mg as

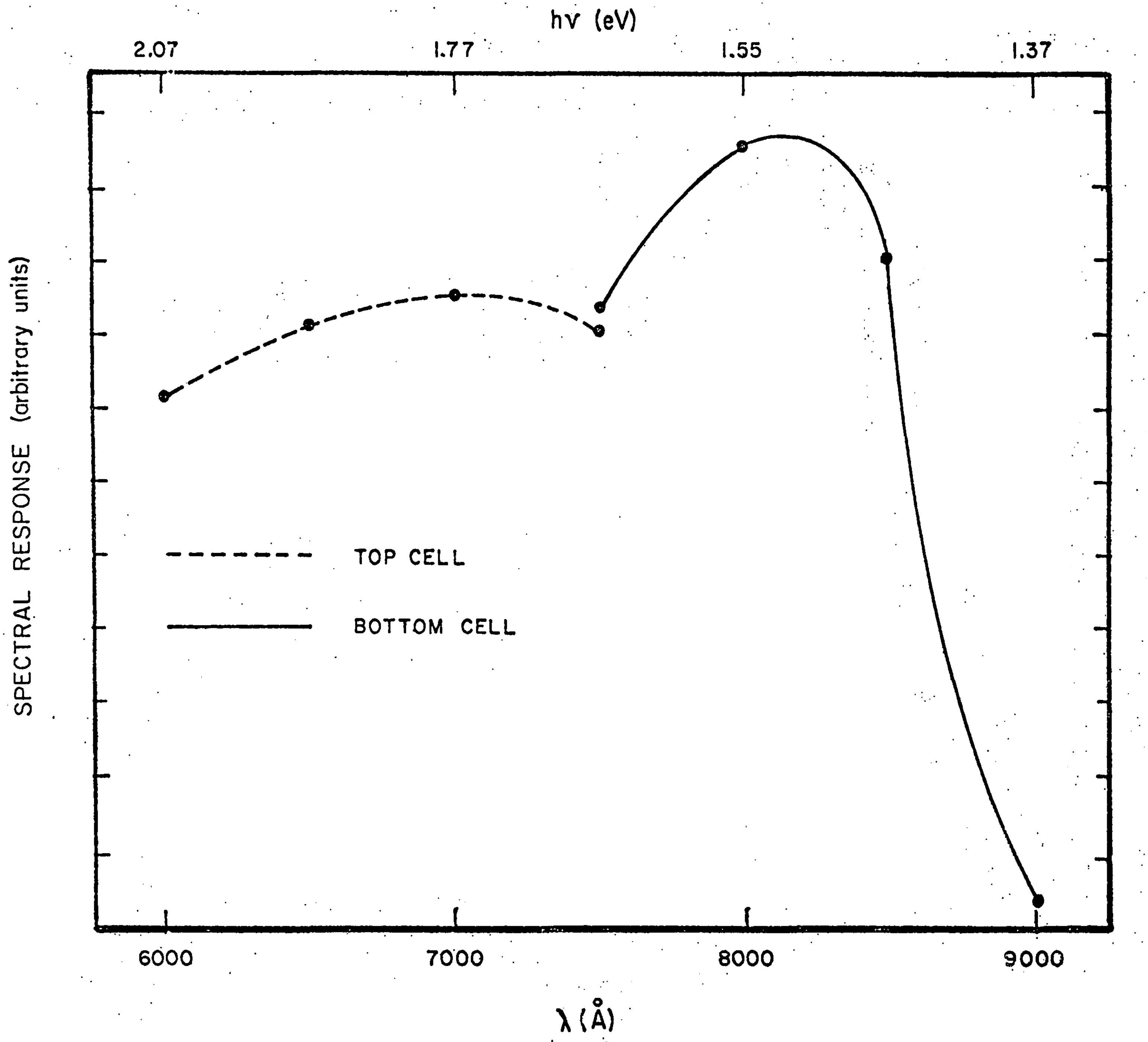

Figure 2. Spectral Response Data For AlGaAs/GaAs Cascade Cell

a dopant and use a capped melt to reduce the effect of the high Mg vapor pressure.

Be can still be used as a dopant, however, if the thickness of the n-AlGaAs layer can be controlled and increased to more than several microns. The growth procedure employed previously was to saturate all the six melts at the same temperature. Thus, for a cooling interval of about 4°C per melt, the later melts such as numbers 5 and 6 would be at a very high degree of supersaturation. Such high supersaturation will produce a lot of solid nuclii in the melt that will compete with the substrate and thus result in an uncontrolled layer thickness. The growth process is now being altered as follows:

> Melts which are to be subjected to a high degree of supercooling (such as n-AlGaAs and the window layer) will be saturated at a lower temperature from a separate source in their slide. The saturation temperature of these melts will be adjusted such that only a few degrees of supersaturation will be present when they come in contact with the substrates.

2. Tunnel Junction Development

Tunnel junctions in AlGaAs with bandgaps up to 1.8 eV have been obtained and are capable of carrying currents up to several amp/cm^2. This is adequate for performance under multi sun illumination.

So far Ge and Be have been the main dopants for the p^+ layer and Te for the n^+ layer. Te has been chosen because of the lack of alternatives that can give highly doped, degenerate levels in this high bandgap material. Unfortunately, the use of Te as the n^+ dopant introduces a problem involving the formations of Te compounds with Al and Ga (Al_2Te_3,GaTe, etc.). These compounds form precipitates that adversely affect the quality of the top cell. The phase diagram of the Al-Ga-As-Te quaternary alloy has not yet been studied.

p^+ (Ge)/N^+(Te) junctions have been grown at 900°C (rather than 800°C) with excellent surface morphology. The improved morphology is attributed to the fact that Te compounds such as Al_2Te_3 and GaTe have melting points below 900°C and thus do not introduce inclusions in the n^+ epilayer. Since heating the tunnel junction after its growth (during the growth of subsequent layers of the structure) is of concern, the cooling rates during growth of top cell and window layers must be fairly fast so that the quality of the tunnel junction will not be adversely affected. When during a recent run the LPE reactor was cooled to room temperature right after the growth process, the tunnel junction exhibited ohmic behavior for a bandgap of about 1.8 eV. In another run when the substrate was kept at 900°C for approximately 20 minutes (time required to grow top cell and window layer), the junction showed rectifying action. This is possibly due to the interdiffusion of impurities at this high temperature. However, the connecting junction retains the desired ohmic properties when held at 800°C for 20 minutes. The use of an alternative n-type dopant such as Se for the tunnel junction will be studied.

3. Window Layer Development

The window layer in this structure is more critical than the single junction AlGaAs-GaAs cell. Window layers with AlAs ≈ 90% have been grown, and Be has been used as a dopant. Zn or Mg cannot be used due to their high vapor pressure and possible contaminations of the other n and n^+ melts. The window layer has to be as thin as possible; so far thicknesses of about 0.5 μm have been obtained. Work on the window layer will focus on controlling the amount of Be doping to prevent excessive Be diffusion into the top cell, and using thin melts for better control of layer thickness.

AlGaAsSb/GaAsSb Material Development

Improved quality AlGaAsSb quaternary layers have been prepared by the "meltback-regrowth" technique. The results obtained by this technique show promise for future work on high bandgap AlGaAsSb p-n junctions. In the past, thin graded layers of AlGaAs have been grown by this method. Briefly, in this technique a melt containing Al, Ga, As, and Sb is prepared in such a way that it is slightly (∿10°C) undersaturated. Then a wafer of GaAs is inserted in this melt so that dissolution of GaAs begins in order to supply As to this melt. At the same time transport of Al and Sb occurs toward the substrate and a layer of AlGaAsSb is deposited on it. In our work such layers have now been grown and can be lattice matched to $GaAs_{1-y}Sb_y$ layers (bottom cell) with y up to 12.5%. A complete analysis of the composition of these layers has not yet been attempted, but clear evidence of lattice grading is obtained from

X-ray diffraction measurements. To be noted is the fact that these layers are grown at a constant temperature and therefore this growth has no detrimental effect on Al depletion in other AlGaAsSb quaternary p-n junction melts. It will be recalled that in earlier experiments such graded layers were grown by using a conventional ramp-cooling approach over a large temperature interval. While graded layers of sufficient quality were routinely obtained, this large cooling tended to deplete Al from the quaternary p-n junction melts. This happens because these melts have to be saturated at their growth temperature (≈760°C) and then are heated to a higher temperature (≈780-790°C) for saturation of the graded layer melt. When the furnace is next ramp-cooled back to 760°C, the Al present in melts tends to form compounds such as GaAlAsSb resulting in little or no Al available for growth of subsequent p-n junctions. Thus, one effectively grows ternary GaAsSb (instead of AlGaAsSb) p-n junctions on AlGaAsSb graded layers.

Work is continuing on this quaternary in effort to obtain layers having longer diffusion lengths.

Work in the GaAsSb ternary has been directed toward reproducing the long collection depth measurements. The results have not been as good as expected; surface morphologies have not been good and collection depths have been around 2 μm.

The open circuit voltage of GaAsSb p-n junctions remains lower than expected for most of the diodes which have been grown. The V_{oc} values are around 0.5 V for a bandgap of 1.2 eV. Diode factors for these diodes have typically been in the range of 1.7 to 2.0, indicating that recombination in the junction depletion region is taking place. The nature of this recombination center is unknown at the present time; it may be either an impurity or a crystalline defect. Differentiation between the two possible sources of recombination is typically quite difficult. Techniques such as SIMS require impurity concentrations of 10^{15} cm^{-3} or greater for identification; low temperature, high resolution photoluminescence has been reported to detect impurities around 10^{13} cm^{-3} or 10^{14} cm^{-3}. TEM techniques can identify clusters of lattice defects which possess dimensions of tens of angstroms, but lacks the resolution for single lattice defects. DLTS gives quantitative information on the energetics of defects but does not give the source of energy levels.

Discussions are currently underway to determine the most advantageous approach to the problem. Defect identification is important so that steps can be taken to reduce recombination centers which adversely affect device properties.

Spectral response data were collected on two $GaAs_{0.9}Sb_{0.1}$ samples which had bandgaps of ∿1.24 eV and collection depths of 2 μm. The response, depicted in Fig. 3 for one of these samples, compared quite favorably with response data published by workers at Varian, Inc., for AlGaAsSb/GaAsSb cells.* The characteristics of the response curves are similar with tailing-off of response with increasing photon energy; this is characteristic of materials with poor n-type diffusion lengths. Even so, the response at 2.2 eV photon energy is approximately 40% of that of the maximum response (1.3 eV photon energy).

GaInP Materials Development

Development of this ternary, which is being considered as a wide bandgap upper cell in GaInP/GaInAs cascade cell materials combination, is continuing using the HCl-hydride open tube VPE growth system.

The leaks which developed earlier in the growth system have been eliminated and new HCl and PH_3 sources were installed. The system has now returned to its initial operating status. Major progress has been made in calibrating the system in terms of composition vs HCl flow rates over the Ga and In sources. One problem that was identified during the composition calibration was a shift in composition that resulted when the In source was not replenished often enough to maintain constant In transport. This has now been corrected.

Figure 4 shows the x-ray diffraction data on a sample in which 5 layers of different compositions were grown consecutively. The first 3 layers are readily visible while the last 2 layers are closely matched to the GaAs and are therefore not identifiable in the x-ray diffraction pattern. These layers were grown by increasing the In content in equal steps as each new layer was grown.

Doping calibration experiments have been initiated but as yet have been limited to GaAs which was deposited on Cr-doped substrates. The first

*Moon et al., 13th IEEE Photovoltaic Specialists Conference, Washington D.C., p 864 (1978).

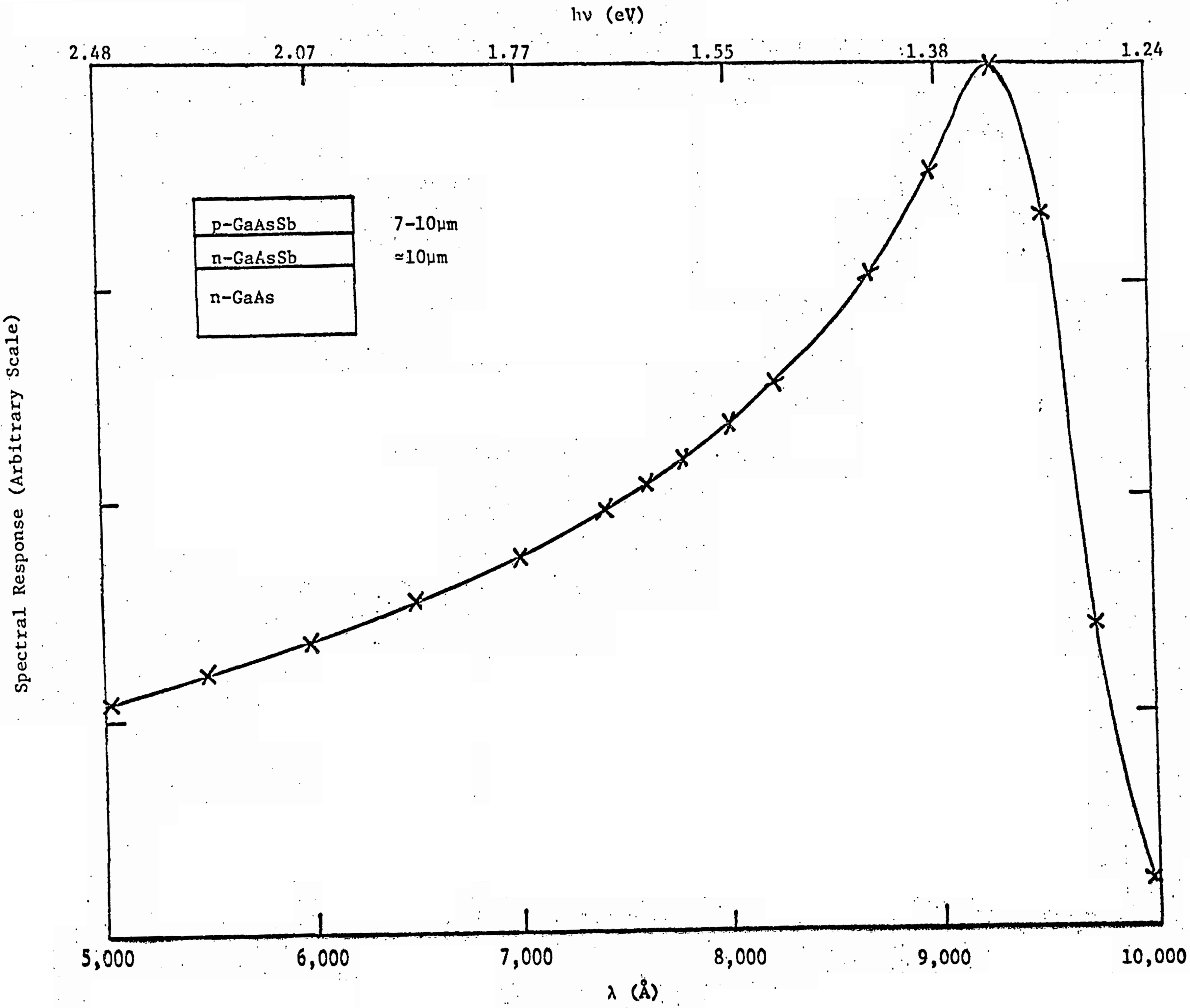

Fig. Spectral Response for GaAsSb p-n Junction

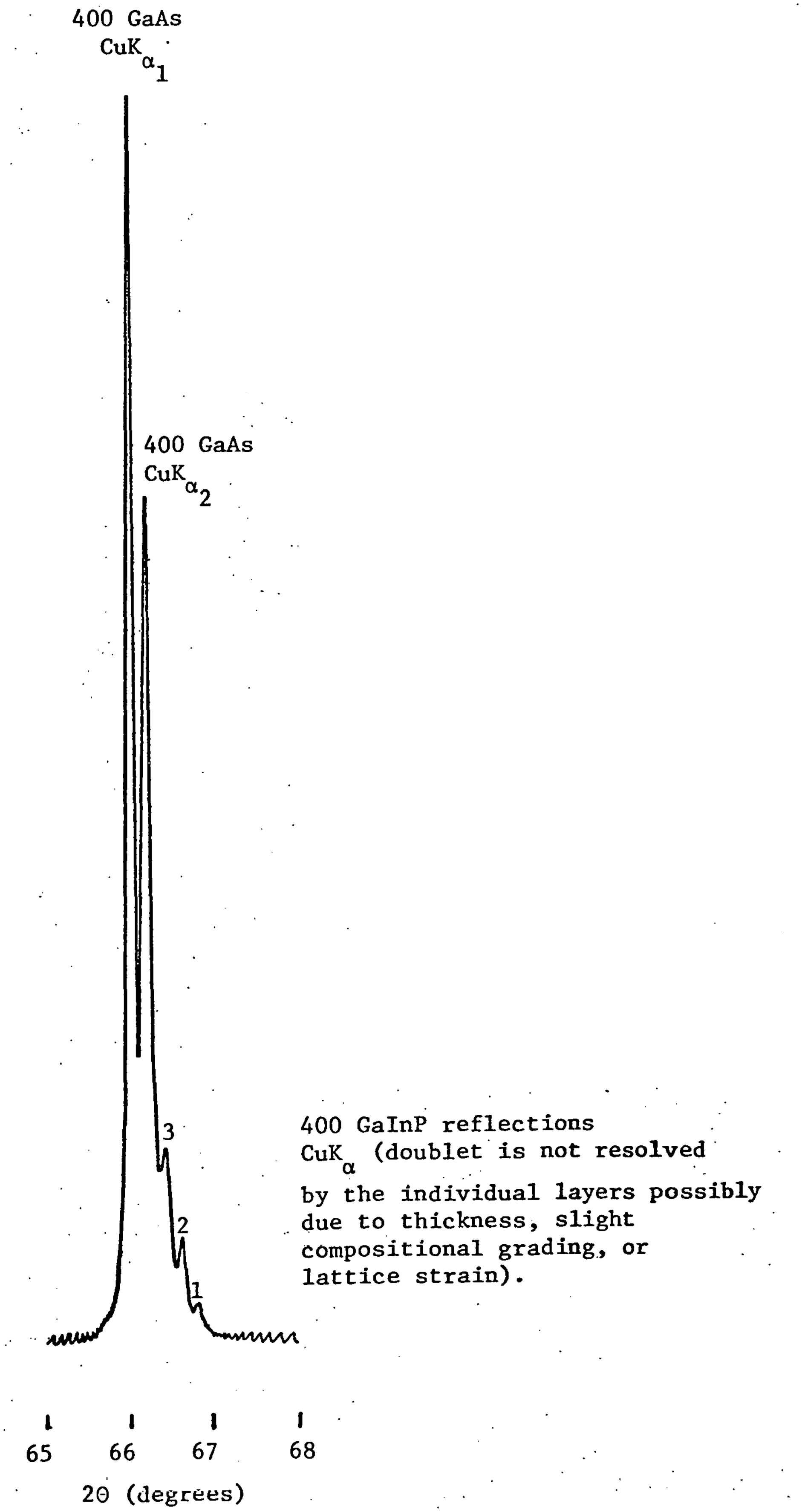

Figure 4. X-ray diffraction pattern of (400) reflections from a 5 layer GaInP deposit on a (100) GaAs substrate. Several layers are easily distinguished and the others are masked by the strong substrate reflection.

step in these experiments was to grow undoped GaAs in order to obtain background carrier concentration information. This will serve as a reference point for the system which is intended to verify reproducibility. The use of a GaInP reference is also planned but is not as reliable as GaAs since the ternary compound represents an additional variable over that of a binary.

Several attempts have been made to form GaInP p-n junctions but were unsuccessful and resulted in an ohmic interface. This may be due to improper carrier concentrations in the GaInP layers or to the presence of a lattice mismatch at the GaInP/GaAs interface.

With the available composition data it is anticipated that GaInP layers suitable for Hall effect measurements can be grown on semi-insulating GaAs which will then provide the needed carrier concentration data. At that point, p-n junction fabrication can proceed with much more confidence.

Inverted Structure Development

A proposed AlGaAs/AlGaAsSb/GaInAs inverted cascade solar cell structure was discussed in detail in the previous Technical Progress Report (dated September 30, 1979). Because of poor GaInAs junction quality, work in this has continued using GaAsSb in place of GaInAs for the lower bandgap cell.

Some work was begun to grow GaAsSb p-n junction layers on graded AlGaAsSb layers, as described previously. On material with a bandgap of 1.2 eV, p-n junctions with $V_{oc} \simeq 0.4V$ were obtained. This rather low value has caused some concern, and additional experiments are required to determine if and how V_{oc} can be improved. Possible approaches are better quality graded layers, slower cooling rates (i.e., lower growth rates) for GaAsSb p-n junction layers. Detailed I-V and collection depth measurements will provide information on the quality of these layers. Hall measurements can be used in conjunction with extensive melt bakeout procedures to determine if the purity of epitaxial layers can be improved.

At present the basic question with the inverted structure is whether or not GaAsSb can be improved to yield acceptable p-n junctions (in terms of V_{oc} and J_{sc}). Therefore, work on the inverted structure per se is being suspended until the GaAsSb materials and junction quality can be improved.

As soon as a definitive (and hopefully favorable) answer is obtained for this question, work can be resumed on the inverted structure if desired. It should be recalled that all the other components for this structure (wide bandgap cell, tunnel junction, lattice-expanding graded layers) have been fabricated here and this technology seems well under control.

MO-CVD Growth System Work

The MO-CVD system being assembled at NCSU for use in studying AlGaAs and GaAlAsSb under subcontract to this project is nearing completion. This system is depicted schematically in Figure 5.

The final temperature controllers for the liquid metal-organic sources have been received and installed. The reaction chamber and loading chamber have been completed and installed. Preliminary leak checking has been completed for the system and the major leaks have been repaired. Preliminary testing of the mass flow controllers has been completed.

Plans for the immediate future are as follows. Installation and checking of the RF generator will be completed. Final helium leak checking will be done on all gas flow lines. Final checking will be completed of all mass flow controllers. The system will then be ready for initial growth runs to begin. These initial runs are expected to begin during the next month.

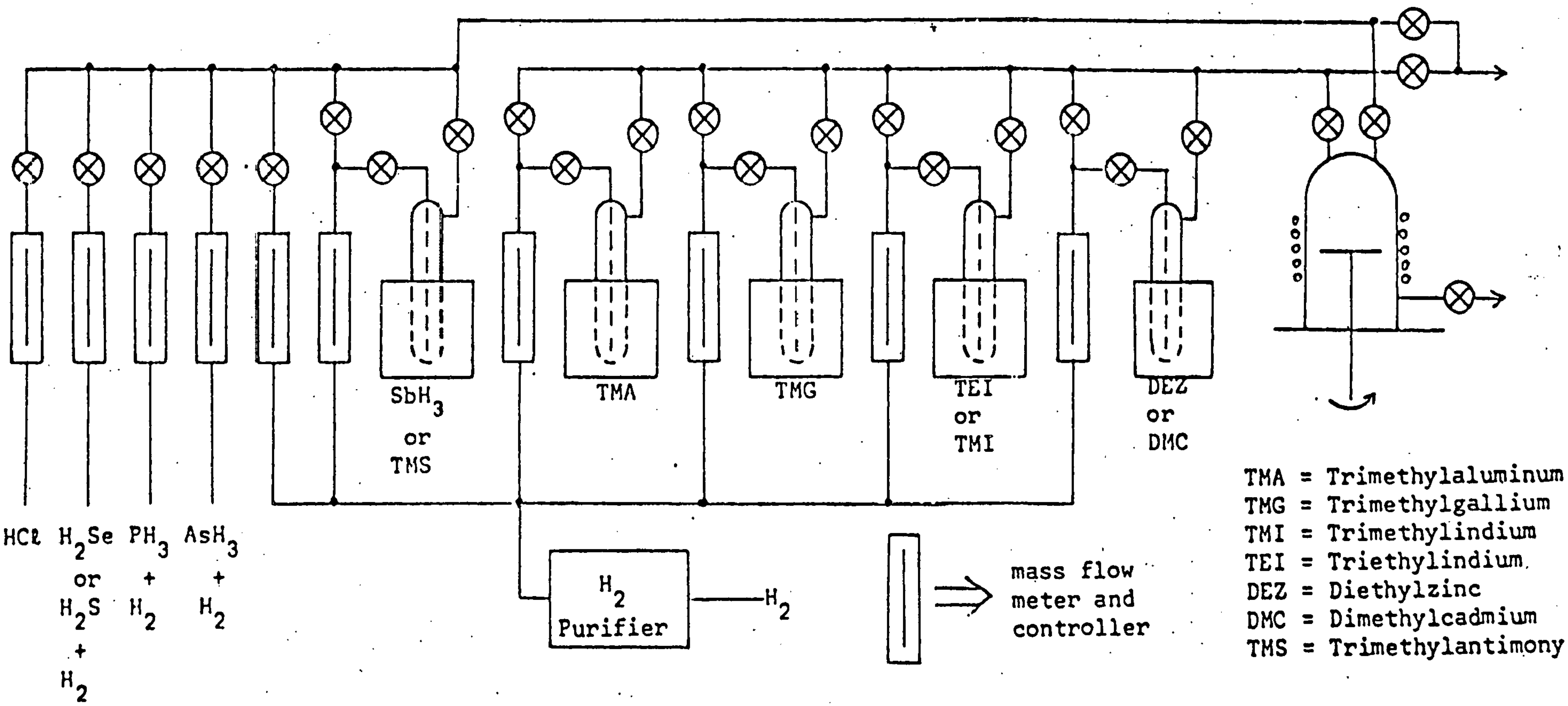

Fig. 5 Gas flow system for a complete MO-CVD III-V Growth System

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