PROGRESS IN THIN FILM GaAs SOLAR CELLS*

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N67-26265
(ACCESSION NUMBER) 19 (PAGES) CR-84014 (NASA CR OR TMX OR AD NUMBER)
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INTRODUCTION

GaAs is attractive as an active material for thin-film solar cells because of its high optical absorption coefficient, and the good match of the bandgap to the solar radiation spectrum. Cells using polycrystalline films of GaAs have been under investigation in our laboratories for some time. Methods for the fabrication of the cells have been evolved, and their operating characteristics have been examined. This paper will review the progress which has been made during the last eighteen months.

P-n junctions formed in polycrystalline films of GaAs have exhibited low shunt resistances. Consequently, a barrier contact structure has been employed for solar cell fabrication. Two cell types have been evolved, as shown in Figure 1. The first of these uses a substrate of molybdenum, and a barrier layer of platinum, with an antireflection layer of SiO. Cells of this type have been made with areas up to 10 cm^2, but the majority of the results reported here were obtained with cells of 2 cm^2 area. The other cell structure has an aluminum substrate, and a barrier layer of cuprous selenide, and the cell areas have been in the range 0.7 to 1.0 cm^2. The results obtained from the development of these two types of cells will be discussed separately.

CELLS ON MOLYBDENUM

Substrate Precoat

As reported earlier,[1] a precoat of Sn-Ge alloy has been developed which allows a low-resistance contact to be formed when GaAs is deposited on molybdenum. This precoat is applied by sequential vacuum evaporation of the alloy components. The effect of the alloy composition on the cell performance has been investigated. Recent results have provided an understanding of the operation of this precoat.

*Research reported in this paper was sponsored by the Aero-Propulsion Laboratory, Research and Technology Division, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, under contract No. AF33(615)-3486, and by the National Aeronautics and Space Administration, Lewis Research Center, Cleveland, Ohio, under Contract Nos. NAS 3-6466 and NAS 3-8510.

It has been found that for low tin concentrations, a non-ohmic high-resistance contact is formed between the substrate and the film. For high tin concentrations, a greater carrier concentration is found in the GaAs film surface region. It appears that the optimum alloy proportions are 50% tin, 50% germanium. It is interesting to see why this should be so.

The phase diagram for the Ge-Sn alloy system is shown in Figure (2). We find that at the temperature of the substrate during GaAs film growth - 800°C - the 50% - 50% alloy lies on the liquidus curve. If the tin proportion is reduced, therefore, some of the germanium will be precipitated as a separate phase on the surface of the molybdenum substrate. This is thought to account for the high-resistance contact which is produced under these circumstances. The fact that the precoat alloy is liquid at the film growth temperature also implies that the GaAs grows by precipitation from a solution in the alloy, and that the growing face is covered by tin and germanium at the start of the deposition process. Consequently the initially grown material will be saturated with tin and germanium, and this is thought to provide the low-resistance contact to the molybdenum. Calculations also show that at the growth temperature, tin will be lost from the substrate by thermal evaporation. This was checked experimentally, and it was confirmed that both the tin and the germanium leave the substrate: the germanium may be transported as germane by reaction with the hydrogen furnace ambient. Hence the precoating technique provides a method for the formation of a GaAs film with low resistivity material against the substrate, and a progressively decreasing impurity concentration as the film thickness increases.

GaAs film growth

Although various alternative GaAs film growth processes have been investigated, the majority of the cells have been made with GaAs films formed by the vapor transport process using GaAs source wafers, with oxygen providing transport by the reaction:[3]

$$2\ GaAs + H_2O \underset{\text{low temp.}}{\overset{\text{high temp.}}{\rightleftharpoons}} Ga_2O + As_2 + H_2$$

A new type of furnace has been developed for the GaAs film growth: this is shown schematically in Figure 3. The principal advantages of this type of furnace are that it uses only quartz components, and that comparatively large-area films can be grown from small-area source wafers. In operation, the

temperature gradient existing in the furnace causes transport of GaAs from source at 900°C to substrate at 800°C. The growth period is 16 hours, to form between 80 and 100 microns of GaAs on two 2 cm^2 cells simultaneously.

Barrier Layer Studies

The platinum barrier layer is applied by vacuum evaporation, to form a film giving about 70% optical transmission. Alternatives to this procedure have been examined.

The diffusion of zinc from a vacuum-deposited layer to form a p-n junction has been found to yield operating cells, but the efficiencies have been lower than those obtained from the platinum barrier cells, the main problem being poor diode characteristics. The use of copper in place of platinum as a barrier layer, to give a lower sheet resistance, yielded cells which degraded upon storage in room ambient: Figure 4 shows the cell characteristics, and the degradation.

Current collection grids, with an integral busbar, are applied by vacuum evaporation of copper. With care, a fine wire can be soldered to this busbar to provide a reasonably strong low-resistance contact. The cell is completed with an antireflection layer of SiO applied by vacuum evaporation.

Cell characteristics

Calculations have been made on the depletion region width and carrier concentration in the active region of the cell, using capacitance-voltage measurements.(4-6) The procedure used has been to evaporate an array of 1 mm^2 platinum dots onto the GaAs film surface, the dots lying on that part of the film to be covered by the busbar on completion of the cell. When the capacitance measurements were finished, the cell was completed by evaporation of the barrier layer, grid-busbar, and SiO, without any etching to remove the platinum dots. Hence the depletion region widths and carrier concentrations which are measured correspond closely to those of the completed cells. The results exhibit a correlation between N_d and V_{oc} for the cells: this is shown in Figure 5. Mechanisms which would give rise to an effect of this type have been considered. The shift in the Fermi level caused by the change in carrier concentration is in the wrong direction to account for the observed V_{oc} variation. The effect of a combination of shunt and series resistances on V_{oc} have been considered: in this case also, the observed voltage change is larger than

can be accounted for by this mechanism. It appears possible that the effect arises from changes in trapping levels at the active surface, but this has not been confirmed.

A correlation between I_{sc} and depletion region width is also observed in the measurements which have been made. This is of the expected form, and has been combined with the results of a theoretical analysis in Figure 6. The experimental points are shown by circles: the scatter is thought to be the result of surface recombination rate variations, since this is particularly sensitive to changes in surface treatment. The curves are calculated for operation under 100 mW cm^{-2} air mass one sunlight, from which 27% of the photons are lost on transmission through the grid and barrier layer. The parameter αL is the product of optical absorption coefficient (α), which may be taken as approximately 10^4 cm^{-1} for light of higher energy than the GaAs energy gap, and the minority carrier diffusion length (L) in the base material. In earlier work, the diffusion contribution to the cell output current was assumed to be negligible, because of the small minority-carrier lifetime in GaAs. The figure shows that this assumption is not wholly valid: the results indicate diffusion lengths of up to 1/3 micron. This implies a mobility lifetime product of around 4×10^{-8} cm^2. Compared to the figure of 2×10^{-5} for single-crystal GaAs, this seems reasonable, and makes evident the effect of the polycrystalline nature of the films.

An efficiency of 3.8% has been achieved in a 2 cm^2 cell. The I-V characteristic for such a cell is shown in Figure 7. This characteristic was obtained under tungsten illumination giving the same I_{sc} value as sunlight of 100 mW cm^{-2}, as extrapolated from sunlight measurements.

Earlier work on the cells showed that an etching step, which produced initially higher cell efficiencies, also caused cell degradation. This has been eliminated by elimination of the etching process, and the cell efficiency reported above approaches the best seen previously only in the etched cells.

CELLS ON ALUMINUM

The cell structure is shown in section in Figure 8.

InAs precoat

A precoat layer of InAs is applied to the aluminum foil, to provide a low-resistance ohmic contact from the substrate to the GaAs film. The thickness

of this layer is 5 microns, and it is formed by vapor transport from a polycrystalline wafer of InAs, by a process similar to that used for the GaAs film growth. The details of the mechanism of operation of the precoat are not known. However, chemical analysis of material deposited on the furnace walls reveals that the indium is mobile during the GaAs film growth, which implies that alloying occurs at the InAs-GaAs interface. Sectioning also indicates that the overlying film crystallites form epitaxially on those of the precoat. This eliminates the layer of very small crystallites of GaAs which are formed immediately adjacent to the aluminum in the absence of the precoat. It is thought to be the junctions at the grain boundaries of these crystallites which are the cause of the blocking contacts when GaAs is formed directly on either aluminum or molybdenum substrates.

GaAs film growth.

GaAs films for these cells are also formed by vapor transport, the principle being that described above for films grown on molybdenum substrates. The furnace details are slightly different, and the operating temperatures are lower. The substrates are held just below the melting point of aluminum, 640°C, and the source wafers are approximately 100°C higher in temperature.

Control of the oxygen concentration during the GaAs film growth has proved to be critical for success. The oxygen is introduced as water vapor, and the necessary control is achieved by mixing pure hydrogen and hydrogen saturated with water vapor before passing the gas through the furnace. The resistivity of the grown layers is governed by the oxygen concentration, higher oxygen concentrations producing higher-resistance films. This effect is presumably due to the introduction of trapping levels by the oxygen impurity, producing the "semi-insulating" form of GaAs by the mechanism described by Blanc and Weisberg.[7] Reduction of oxygen concentration slows the GaAs film growth rate, so that a compromise must be reached where a reasonably thick film can be formed with a resistance sufficiently low not to impair cell performance. A 22-hour growth period is normally employed, to produce a film 15 microns in thickness.

This film is polished by etching in a dilute solution of bromine in methanol, to prepare the surface for the barrier layer deposition.

Barrier layer formation.

The barrier layer is formed by flash evaporation, under vacuum, of a non-stoichiometric form of cuprous selenide. The starting material has a composition of $Cu_{1.85}Se$, determined by chemical analysis. The actual stoichiometry of very thin layers depends critically upon the flash evaporation conditions. This point has been analysed by Ellis[8], and we shall not pursue the matter further at this time.

Specimens of cuprous selenide formed on glass slides have been used for measurements of optical transmission and electrical resistance. For cell fabrication, these monitor specimens show optical transmission of 60 to 70% to 1.5 eV radiation, and sheet resistances down to 12 ohms per square.

Multiple-beam interferometry methods have been used to measure the refractive index of the cuprous selenide films on glass. These measurements indicate a refractive index of 2.4 at 5460Å. Working from this value, an antireflection layer has been designed. Appropriate calculations based on the methods of Heavens[9] show that a $\lambda/4$ layer of cuprous selenide, followed by a $\lambda/4$ layer of magnesium fluoride, should give the desired result. This has been verified experimentally, with barrier-layer cells on single-crystal GaAs showing I_{sc} increases of 25% over cells without MgF_2.

Cell stability.

In some instances, cell degradation has been observed in cells stored in air. The characteristics of a degraded cell are shown in Figure 10. The effect is apparently caused by the presence of two series diodes in opposition. It has been found that these characteristics can be returned to normal by etching the cells in dilute nitric acid, the results also being shown in the figure.

Ellis[8] has postulated that cuprous selenide films with a stoichiometry between $Cu_{1.85}Se$ and Cu_2Se tend to form a surface layer of cuprous oxide, the remaining cuprous selenide going to the $Cu_{1.85}Se$ stable form. This is confirmed by the results of Heyding[10]. The effect is illustrated in Figure 10. We believe that the cell degradation which we have seen is due to the formation of such an oxide layer. The excess copper in the films would be the result of the loss of selenium during flash evaporation, by the accommodation coefficient effects considered by Ellis. The acid etch apparently removes this oxide layer, restoring the cell to its normal state. We also have evidence that the degradation can be prevented by etching the cells immediately after their fabrication, but we have not yet had an opportunity to run the necessary life tests to conclusively establish this point.

Characteristics and efficiency.

The characteristic of a typical cell is shown in Figure 11. Perhaps the most striking thing about this characteristic is the rectification ratio, a value of 1000 to 1 at 1 volt being typical. The efficiency of 3% is also the mean figure for our present production process, the best value obtained to date being 4.2%.

The cells are very light-weight, the best cell having a power-to-weight ratio of 135 watts per pound under 140 mW cm^{-2} illumination. The cells are somewhat flexible, and can be cut with scissors or a scalpel, such an operation being part of our normal processing.

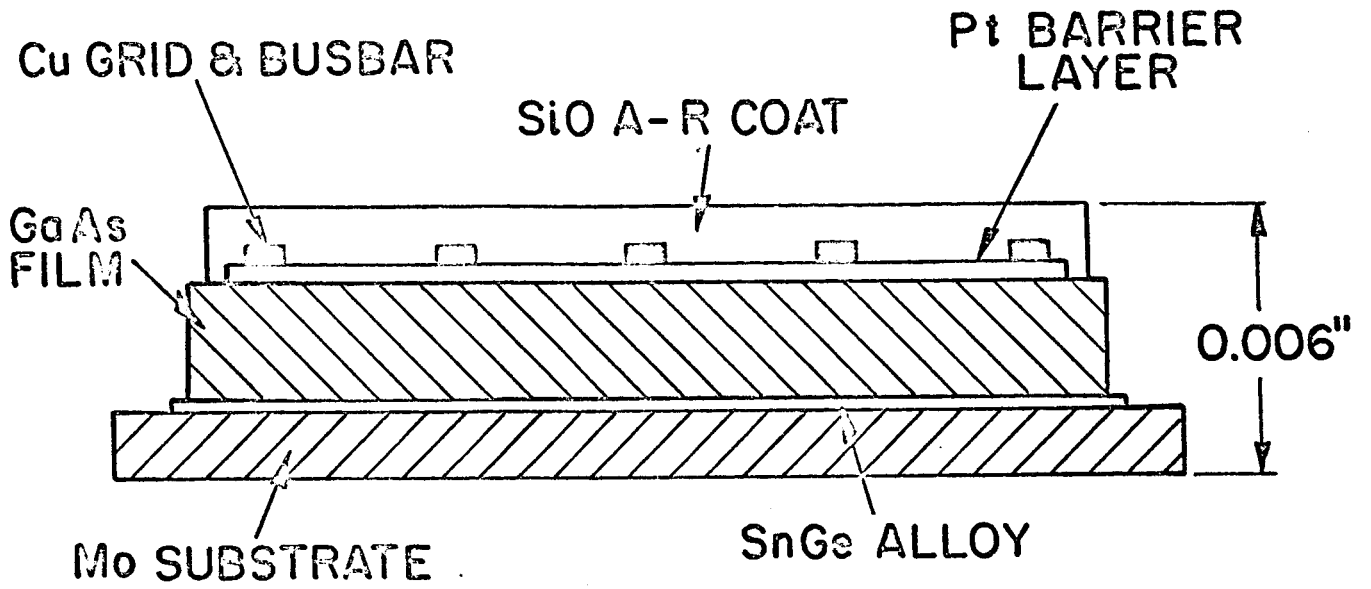
DISCUSSION

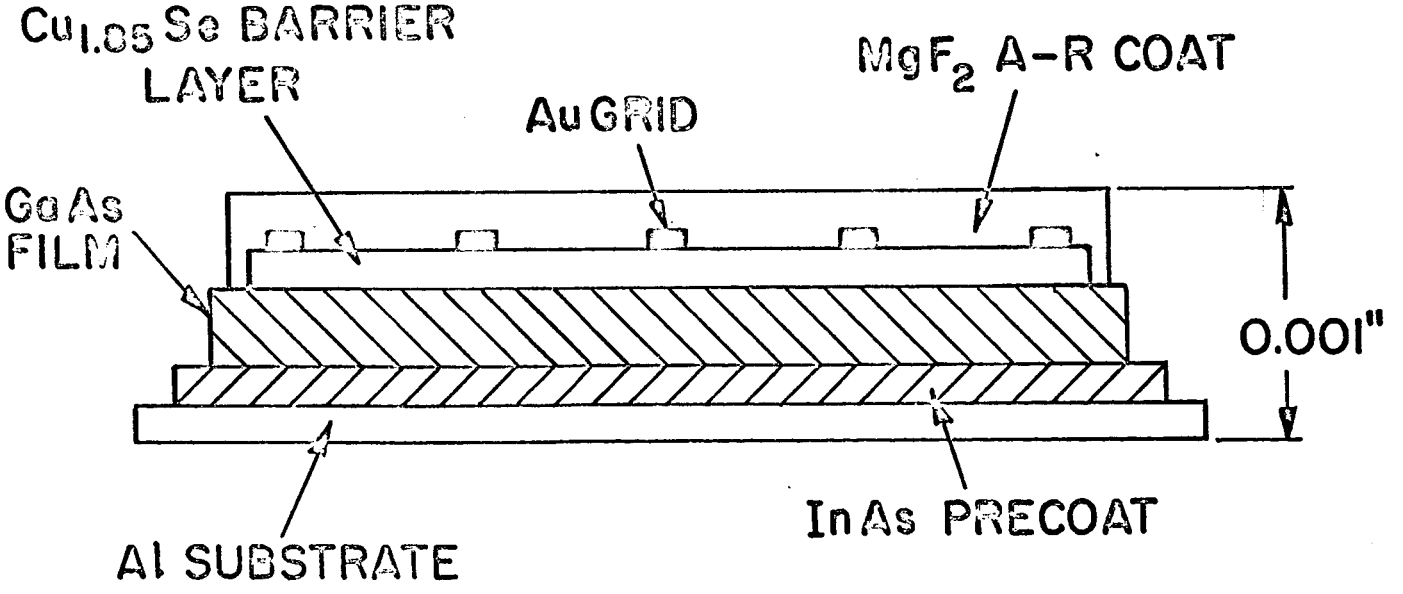
The cell types which have been described are in different states of development. The cells on molybdenum have areas which are approaching the practical range, and the cell configuration and contacting techniques have been developed. The cells on aluminum have more modest areas, but because of their more advanced design hold greater promise for providing low-weight power systems.

One problem is possessed in common by these cells and by most other thin-film polycrystalline cells. This centers on the low V_{oc} values which are obtained, compared with the V_{oc} values for single-crystal cells of the same materials. It would appear that this problem is a most fruitful field for further study, and if suitable surface treatments can be developed to improve the V_{oc} values, thin-film cell efficiencies will be increased considerably.

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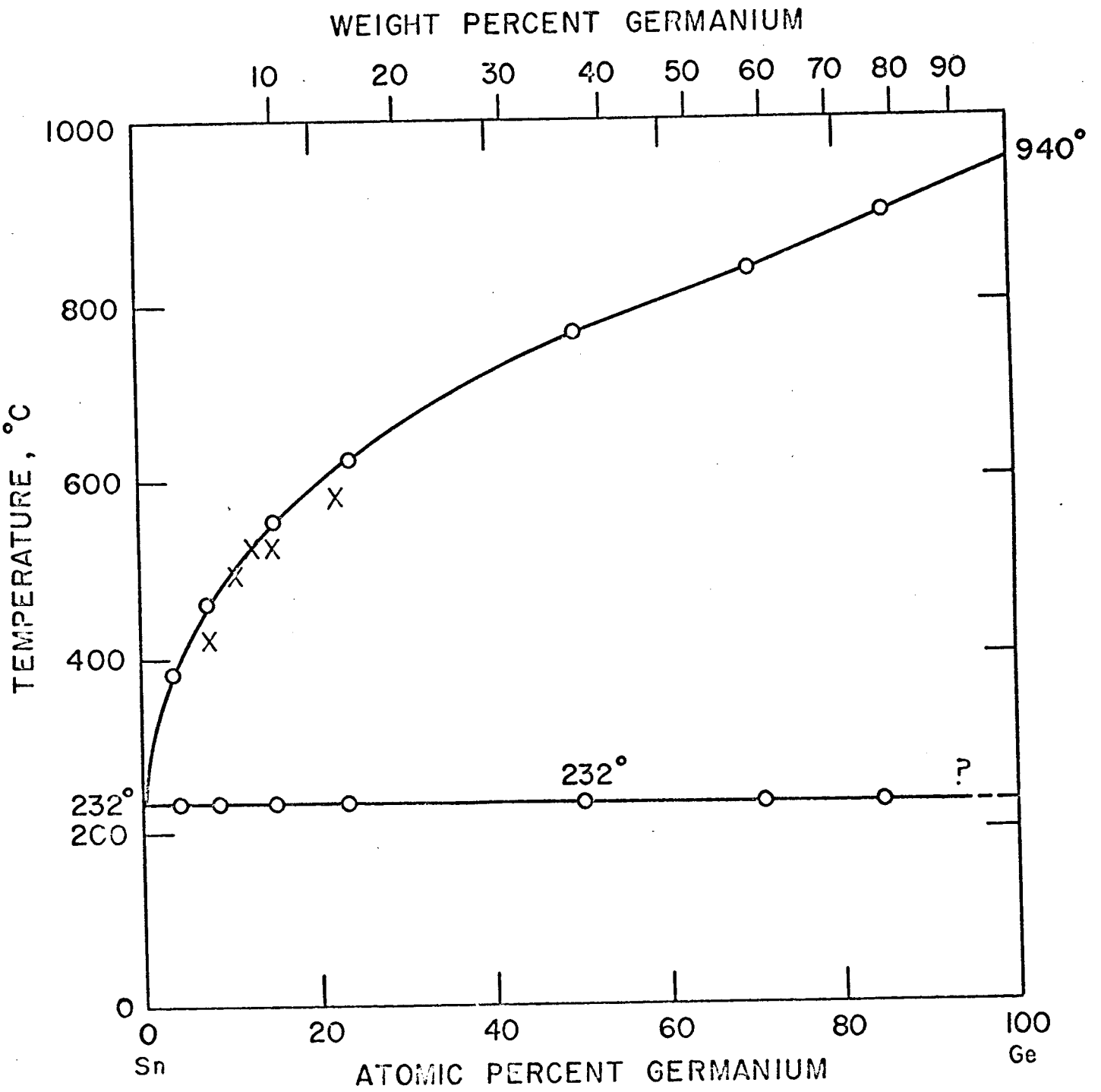
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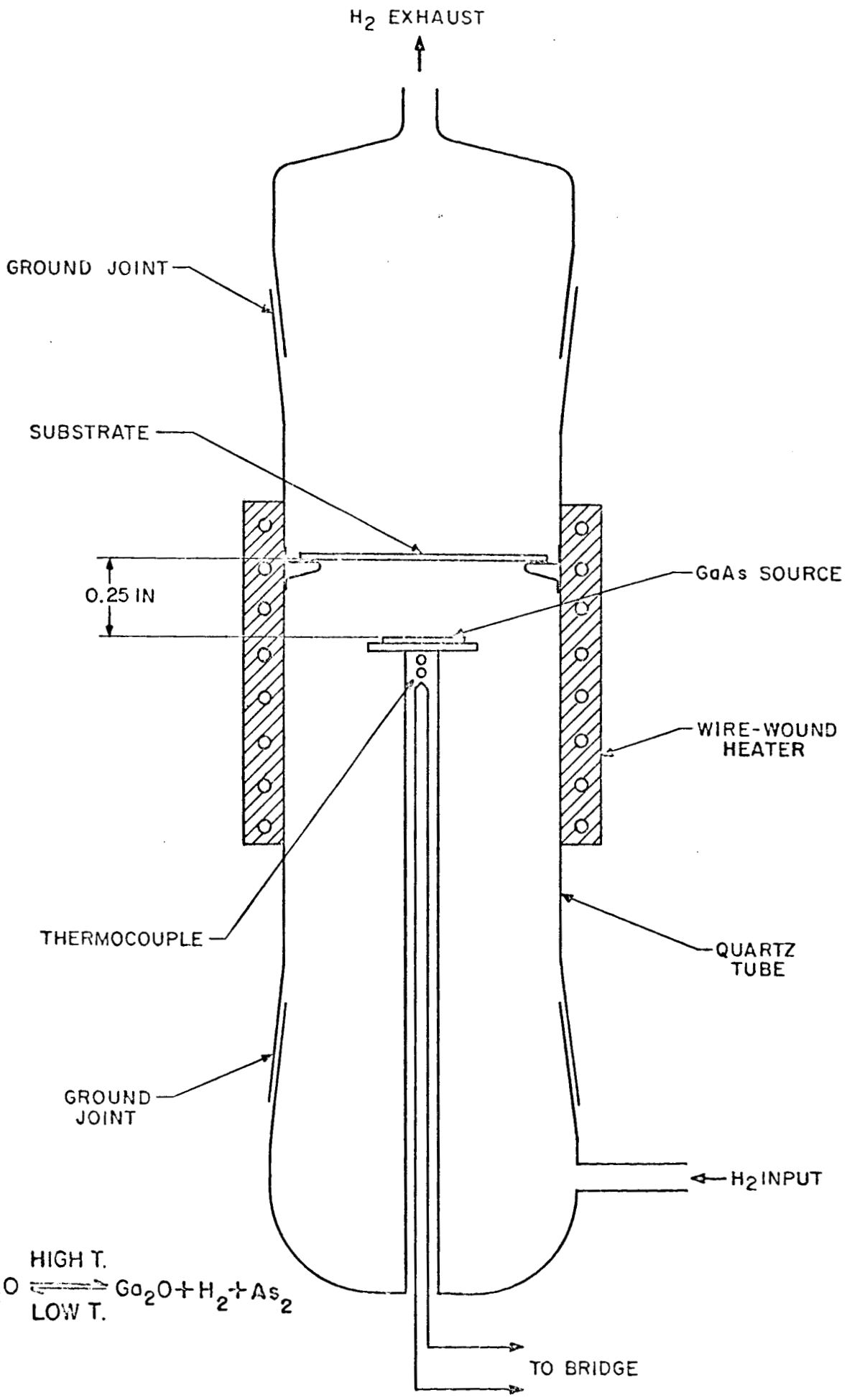




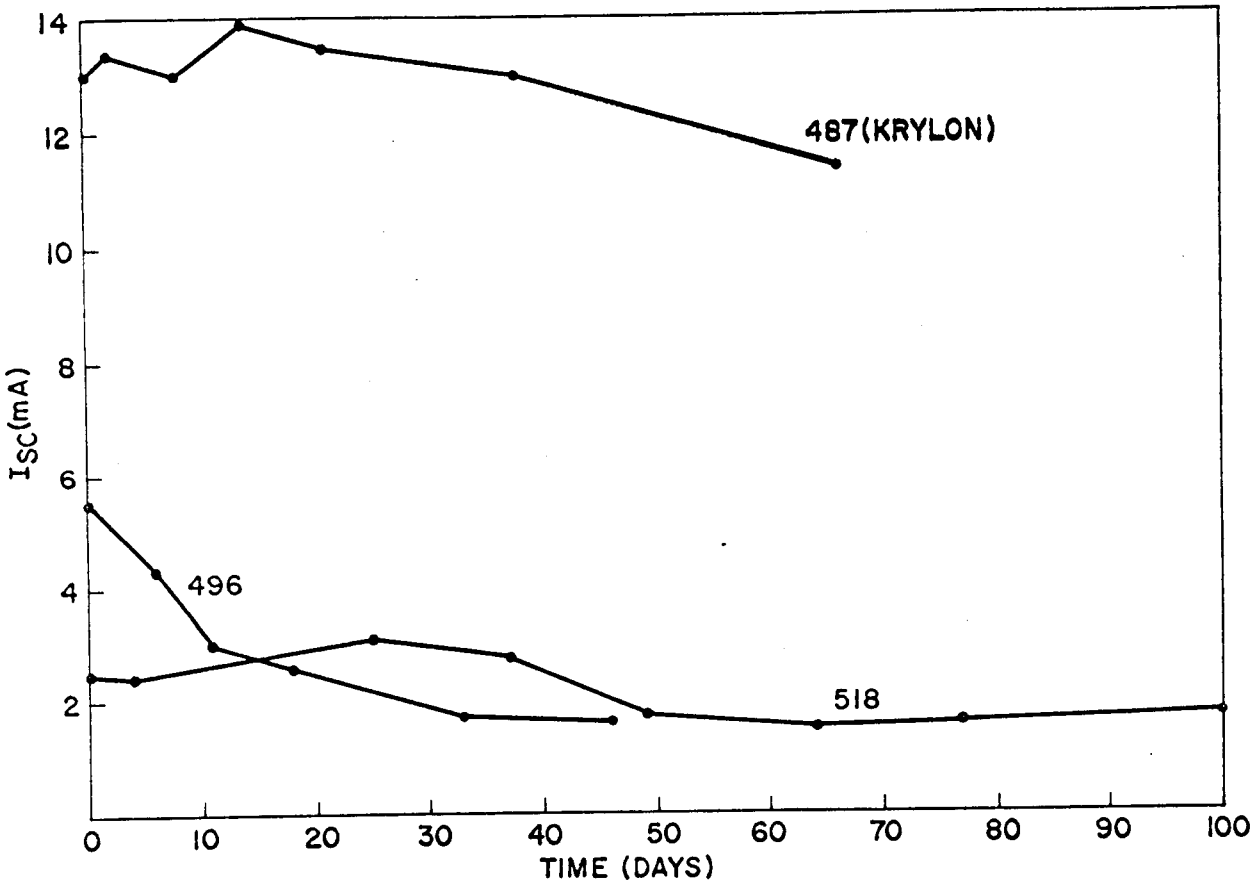
THIN-FILM GaAs SOLAR CELL STRUCTURES

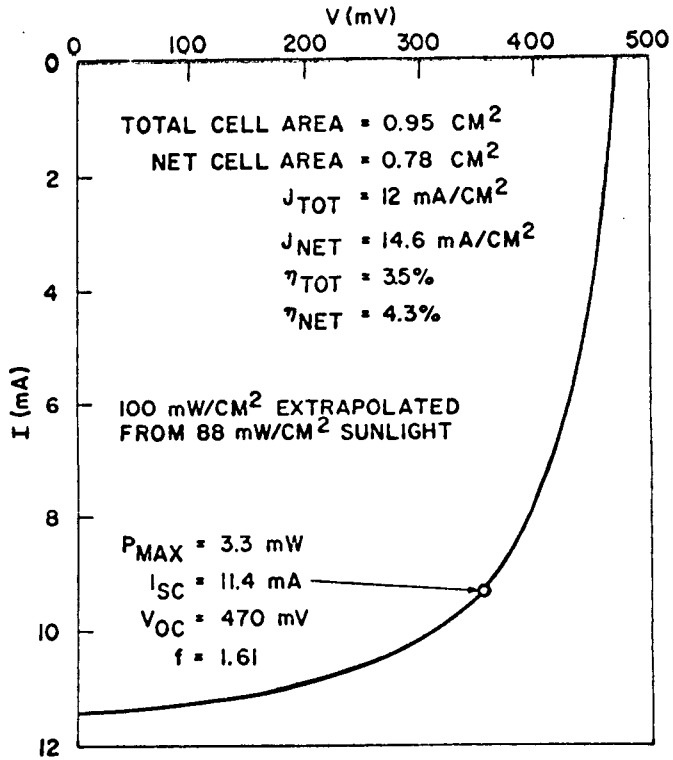
QTR-3

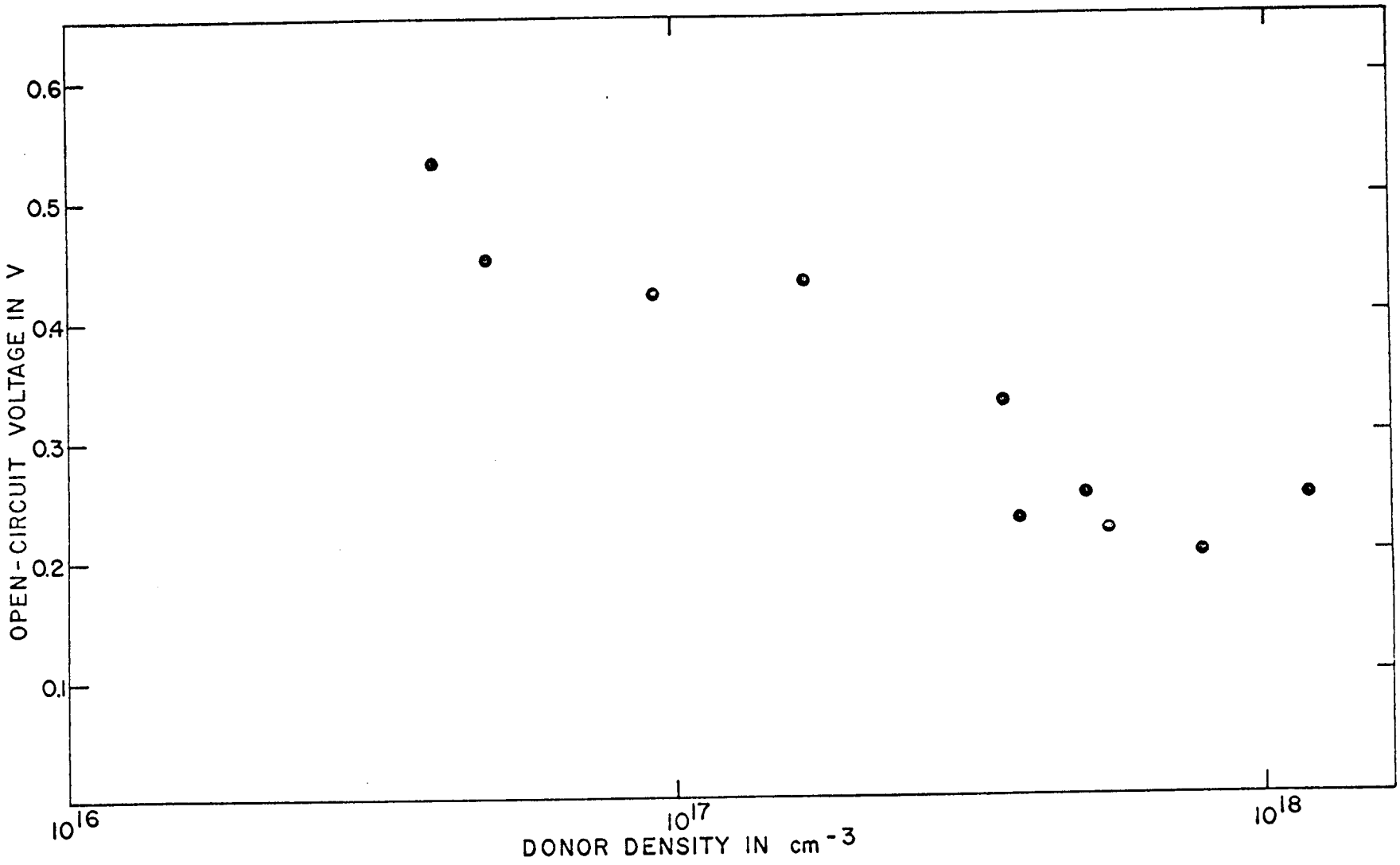

WEIGHT PERCENT GERMANIUM
10
20
30
40
50
60
70
80
90
1000
800
600
400
232°
200
0
940°
232°
?
TEMPERATURE, °C
0
20
40
60
80
100
Sn
Ge
ATOMIC PERCENT GERMANIUM

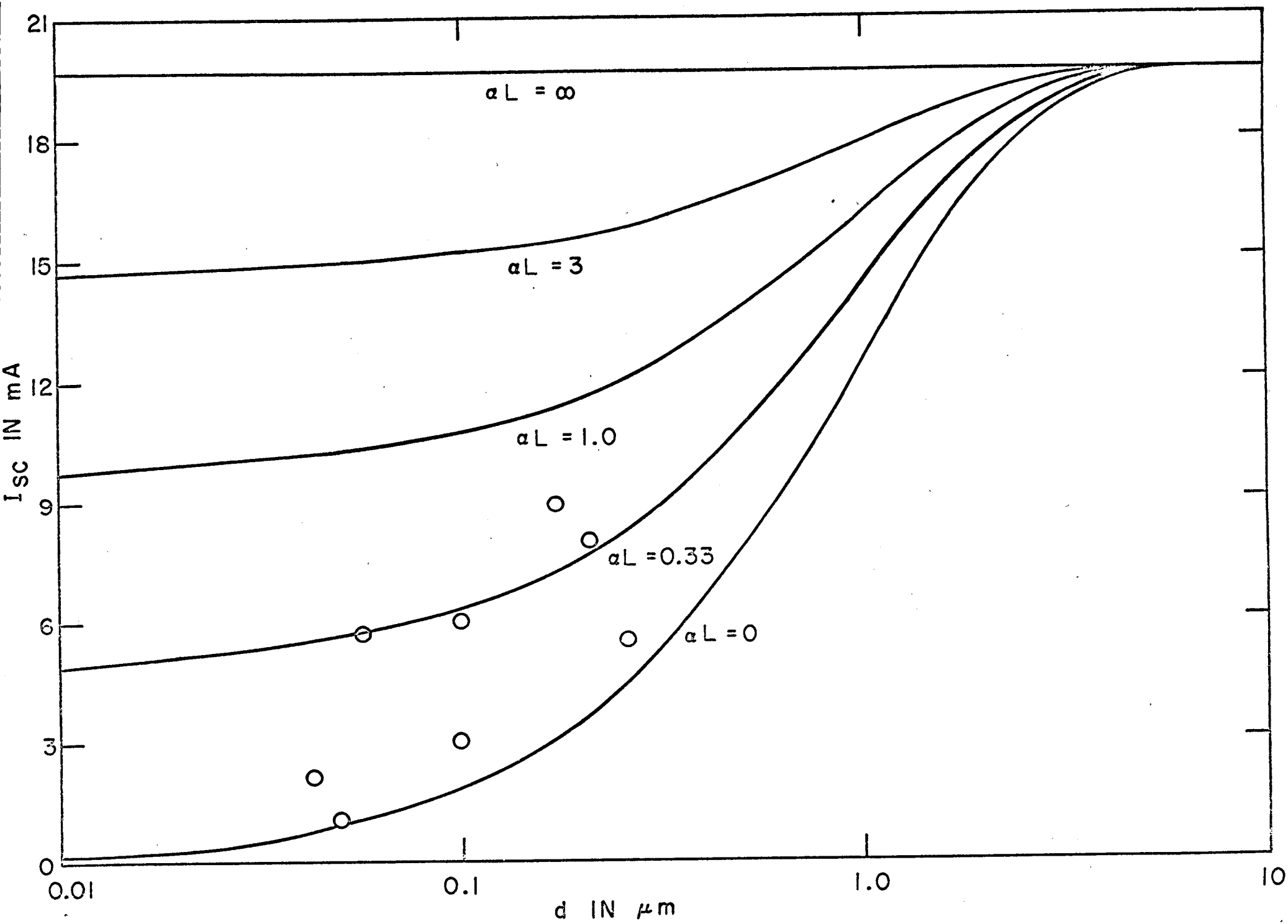


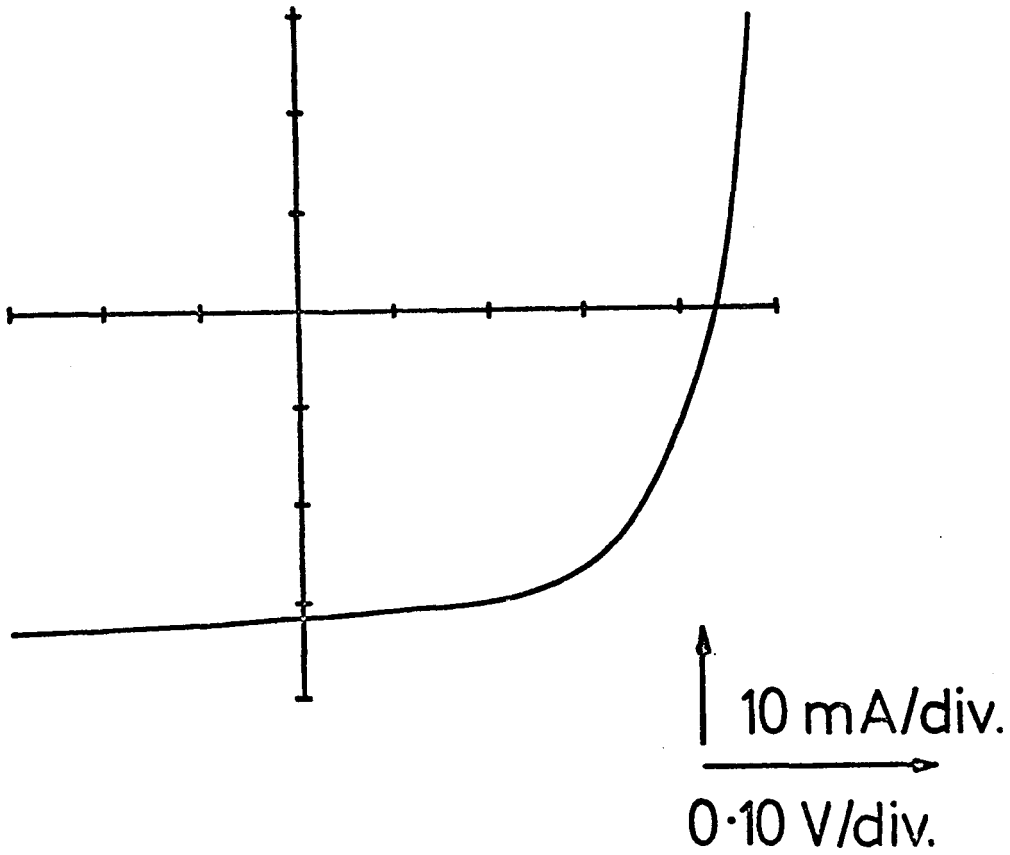
$$2GaAs + H_2O \underset{\text{LOW T.}}{\overset{\text{HIGH T.}}{\rightleftharpoons}} Ga_2O + H_2 + As_2$$


14
12
10
8
6
4
2
I_{SC}(mA)
487(KRYLON)
496
518
0
10
20
30
40
50
60
70
80
90
100
TIME (DAYS)

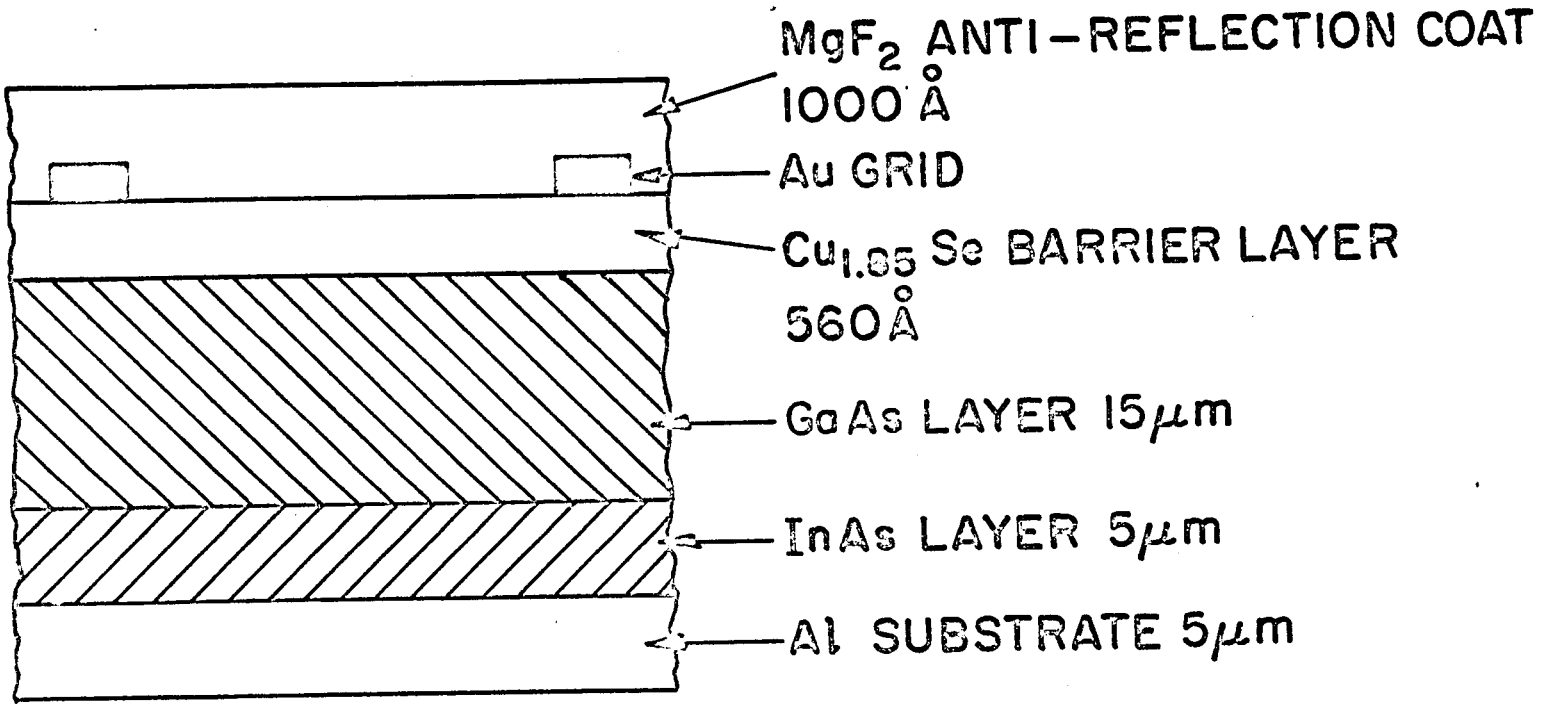

V (mV)
0
100
200
300
400
500
0
2
4
6
8
10
12
I (mA)
TOTAL CELL AREA = 0.95 CM^2
NET CELL AREA = 0.78 CM^2
J_{TOT} = 12 mA/CM^2
J_{NET} = 14.6 mA/CM^2
η_{TOT} = 3.5%
η_{NET} = 4.3%
100 mW/CM^2 EXTRAPOLATED
FROM 88 mW/CM^2 SUNLIGHT
P_{MAX} = 3.3 mW
I_{SC} = 11.4 mA
V_{OC} = 470 mV
f = 1.61


0.6
0.5
0.4
0.3
0.2
0.1
OPEN-CIRCUIT VOLTAGE IN V
10^{16}
10^{17}
10^{18}
DONOR DENSITY IN cm^{-3}

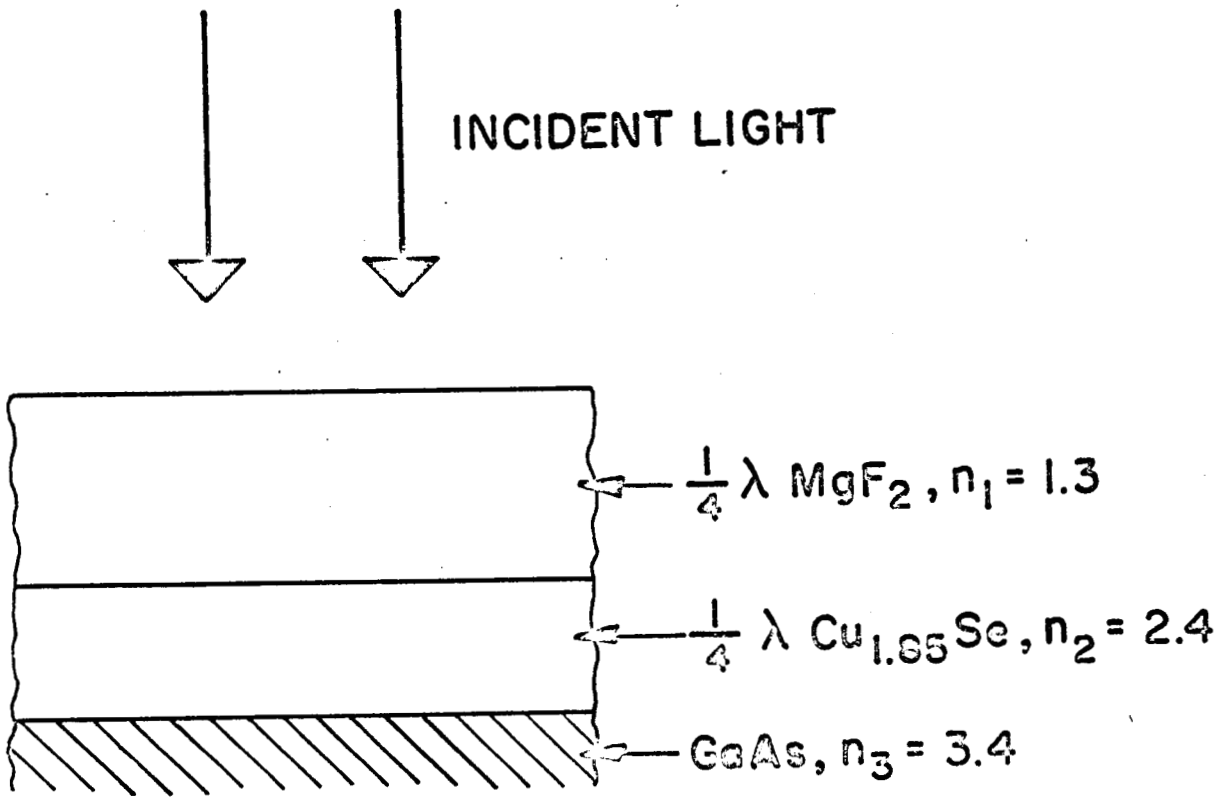

21
18
15
12
9
6
3
0
I_{SC} IN mA
αL = ∞
αL = 3
αL = 1.0
αL = 0.33
αL = 0
0.01
0.1
1.0
10
d IN μm



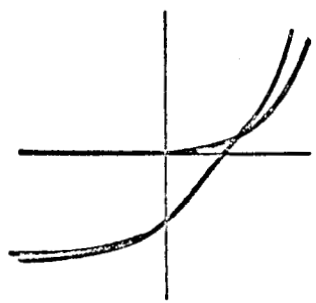
I-V CURVE FOR Pt-GaAs CELL



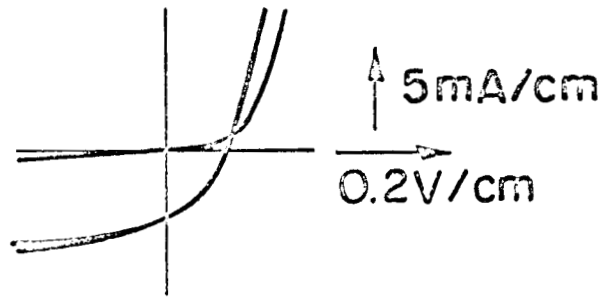
SECTION OF GaAs THIN-FILM SOLAR CELL
ON ALUMINUM SUBSTRATE



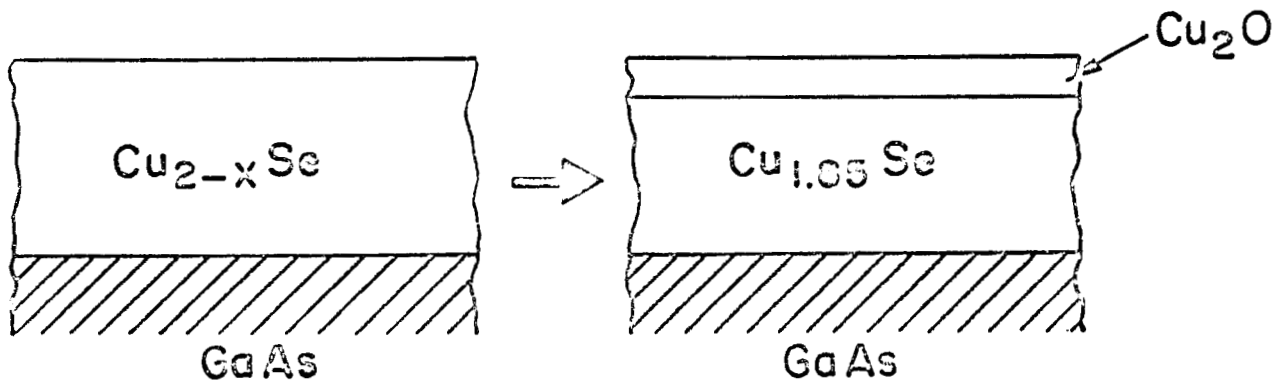
STRUCTURE OF ANTI-REFLECTION LAYERS



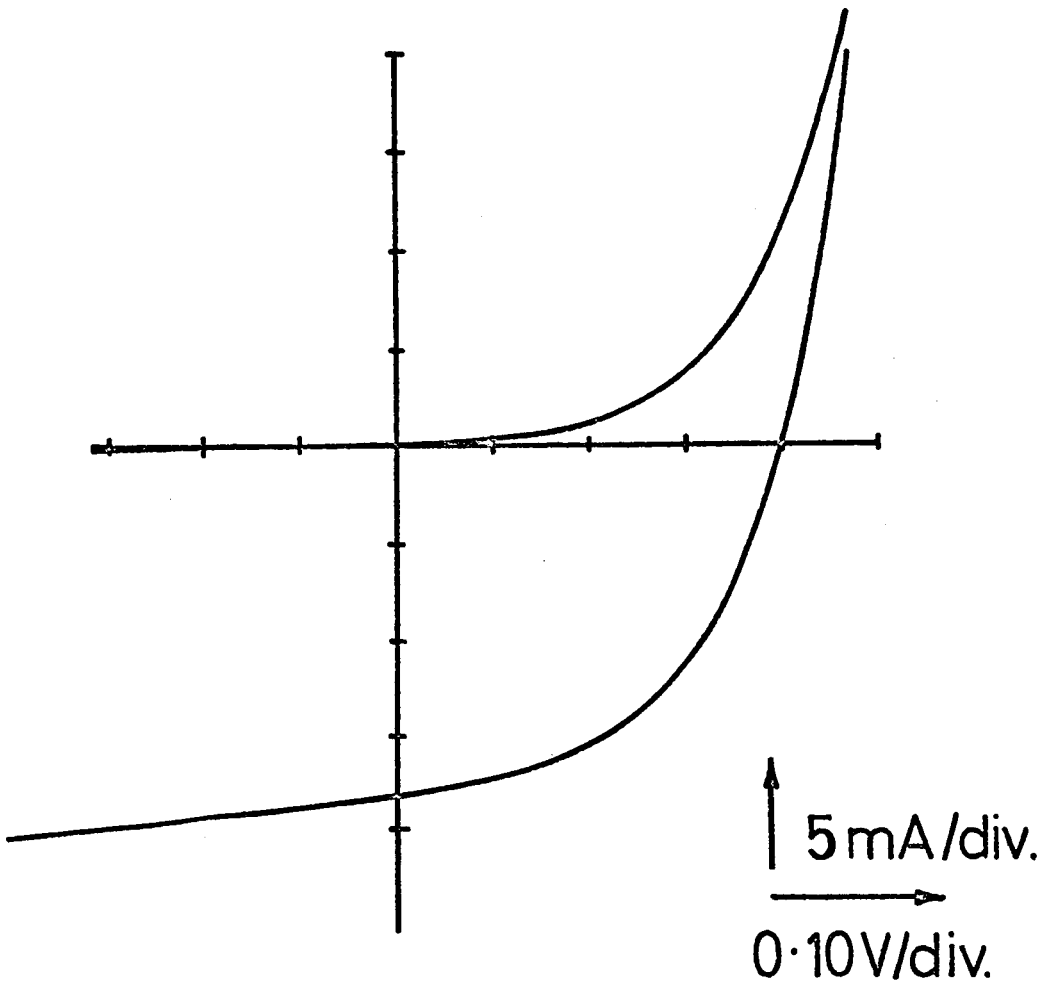
DEGRADED I–V CURVE



SAME CELL AFTER ETCHING



DEGRADATION OF $Cu_{1.8}Se$ CELL



I-V CURVE FOR $Cu_{1.8}Se$ CELL