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STUDY OF SEMICONDUCTOR HETEROJUNCTIONS

OF ZnSe, GaAs and Ge

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ABSTRACT

The fabrication problems and device characteristics of Ge-GaAs and ZnSe-GaAs heterojunctions are being studied.

Heterojunction transistors of nZnSe-pGaAs-nGaAs are described. The nZnSe emitter is epitaxially grown upon (111) or (100) n-type GaAs collector material. The GaAs base region is formed by diffusing zinc through the grown ZnSe into the GaAs. The effects of emitter injection efficiency, base transport factor, and crystal orientation on common-emitter current gain are presented. ZnSe-GaAs emitter-base current-voltage characteristics are dominated by space charge flow in the high resistivity ZnSe emitter. Current gains as high as 35 have been observed. The gain increases with injection level and with increase of the ZnSe resistivity. Decreased base widths, in the range 2 μm to 0.2 μm, also give improved current gain. The gain is low when (100) ZnSe-GaAs interfaces are used.

Heterojunction solar cell performance calculations are also discussed. It is suggested that a heteroface structure might improve the performance of a GaAs np solar cell.

1. INTRODUCTION

During the past few years reports on heterojunction transistors have appeared in the literature. These devices make use of a large band-gap semiconductor emitter (n type) and a smaller band-gap base and collector semiconductor. The difference in band-gap appears as an energy barrier in the valence band which prevents reverse hole injection from a p-type base into an n-type emitter and thereby increases the electron injection efficiency of the emitter over that of a homojunction transistor with comparable emitter doping levels (Kroemer 1957). Thus, high-gain transistor performance can be expected with the ratio of the emitter doping level to base doping level much less than required for a homojunction transistor. Increased base doping may be expected to give better frequency response and reduce emitter crowding.

In the heterojunction transistors fabricated to date (CdS/Si, Brojdo 1965; CdS/Si, Zuleeg 1966; GaAs/Ge, Jadus and Feucht 1969; ZnSe/Ge, Hovel and Milnes 1969) the best current gains tend to be in the range 10-50. The gain appears to be limited by defect components of emitter current caused by interface states or defects near the interface. In the present state of heterojunction research, fabrication problems such as masking and contact technology have not been solved and so no attempts have been made to create structures that might be expected to have high frequency response. Analysis shows that if contact and other fabrication problems can be solved, heterojunction transistors could have about twice the frequency response of a homojunction transistor of comparable dimensions (Ladd and Feucht, 1970). Another reason for interest in heterojunction structures is that their optical properties should be different than that of homojunctions, because of the window effect for photons of energy between the energy gaps of the two semiconductors.

2. ZnSe-GaAs HETEROJUNCTION TRANSISTORS

2.1 Fabrication

Single-crystal layers of ZnSe doped with Ga were epitaxially grown upon (111)B and (100) oriented n-type GaAs substrates using an HCl close-spaced transport process (Hovel and Milnes 1969a). The grown ZnSe layers were from 2 to 6 microns thick with resistivities about 10^6 ohm-cm. The resistivity was high because the growth temperature (640°C) allowed Zn vacancy acceptor creation which compensates most donors. The ZnSe resistivity was reduced to a lower level by diffusing zinc through it during the base fabrication step which followed. p-type base regions in the GaAs were formed by diffusing zinc from the vapor phase through a protective 500-1000Å SiO_2 layer through grown ZnSe into the $1\text{-}5\times10^{16}\,cm^{-3}$ (Sn or Te) n-type substrate-collector GaAs. Diffusion was at 625°C-700°C for times of 5 to 30 minutes, after which the heterojunction sample was quickly quenched to room temperature to prevent any Zn outdiffusion which would increase the ZnSe resistivity. This process yields base widths from 0.1 to 1.0 μm and lowers the ZnSe resistivity from 10^6 ohm-cm to 10^3 ohm-cm. The SiO_2 layer acts both as a mask to Zn indiffusion during diffusion and to Zn outdiffusion during quenching. The GaAs surface is not attacked by either the growth process or the Zn diffusion and provides for planar base regions. The quenching process does not crack the ZnSe layers unless they are more than 4 microns thick.

The Zn concentration in the GaAs at the emitter side of the base ranged from $10^{17}\text{-}10^{18}\,cm^{-3}$ as estimated from resistivity measurements, assuming constant mobility, and assuming a complementary error function distribution for the diffused Zn atoms in the GaAs. This corresponds to base sheet resistances of 500-2000 ohm/cm^2. A curve tracer plot of the p-n base-collector junction voltage-current characteristic is shown in Fig. 1. The forward characteristic is of the form

$$I_C = I_o \exp\left[\frac{qV_{BC}}{\eta kT}\right] - I_o \qquad (1)$$

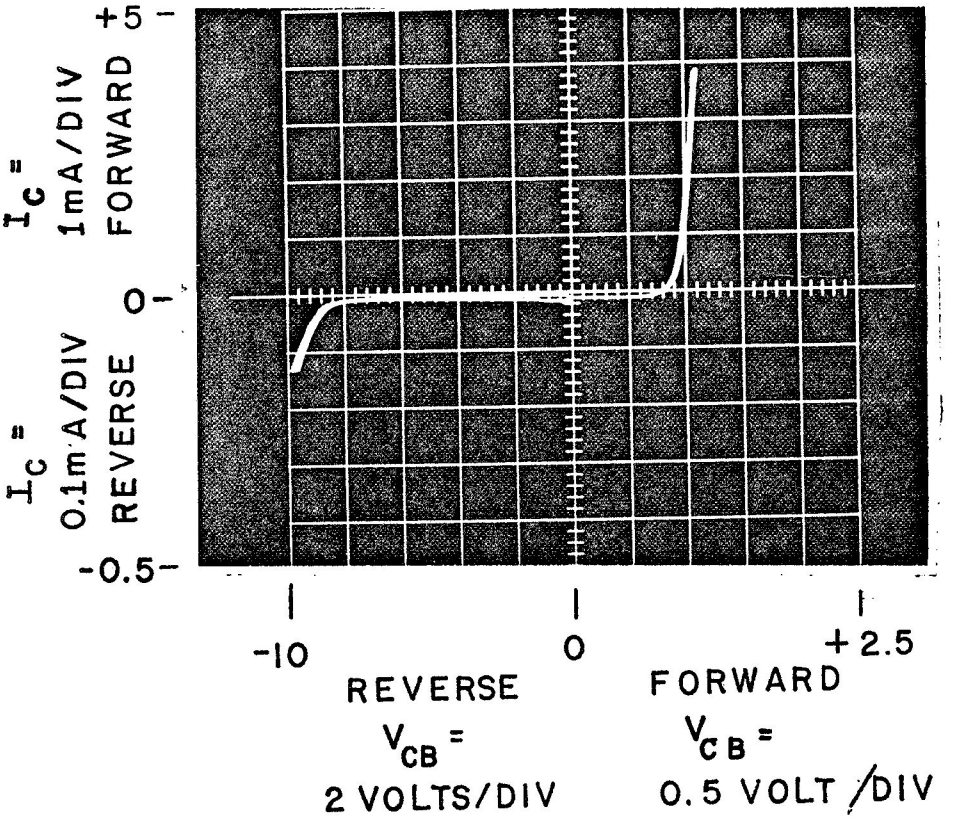


Fig. 1 Typical GaAs collector-base characteristic.

Note the change in scales in going from forward to reverse. (Transistor TR-8-A-1)

where $1.8<\eta<2.2$. The reverse characteristic follows a power law dependence (before breakdown)

$$I_C = BV_{BC}^N \tag{2}$$

where $1.5<N<2.0$.

Figure 2 shows a typical transistor structure. After the Zn diffusion the collector and base regions are exposed by selective etching in 5% bromine-methanol and concentrated HCl respectively. Also the emitter is etched down to 1-2 microns with bromine-methanol to remove any compensated surface layers. Contact to the collector is made with a Sn dot alloyed at 350°C while an In-1% Zn dot alloyed at 280°C makes contact to the p-region. The ZnSe is contacted with a pure In dot alloyed at 300°C. All contact processes use 2-10% HCl gas in H_2 as a flux. Electrical measurements are made by contacting the alloyed dots with tungsten probes. Successful contact to 0.1 μm base regions has been made by this method.

2.2 Emitter Base I-V Characteristics

The theoretical band structure of an npn ZnSe-GaAs transistor biased for operation is shown in Fig. 3. Also shown are interface states, traps in the ZnSe, and the various defect emitter current components which result from the interface states and traps. The emitter current is dominated by space-charge flow at moderate injection levels since the ZnSe resistivity is never lower than 10^3 ohm-cm. Traps in the ZnSe influence this type of current flow very strongly and cause the current to have various voltage dependences (Hovel and Milnes 1968). At or near the interface traps can serve as capture centers for electrons which then tunnel into interface states to recombine. As the emitter current approaches the interface, we may postulate that it splits into three major components. They are (1) the interface state recombination current J_s, (2) the capture-tunnel current J_r, and (3) injected current J_n. It is this injected current, J_n, which provides for transistor action,

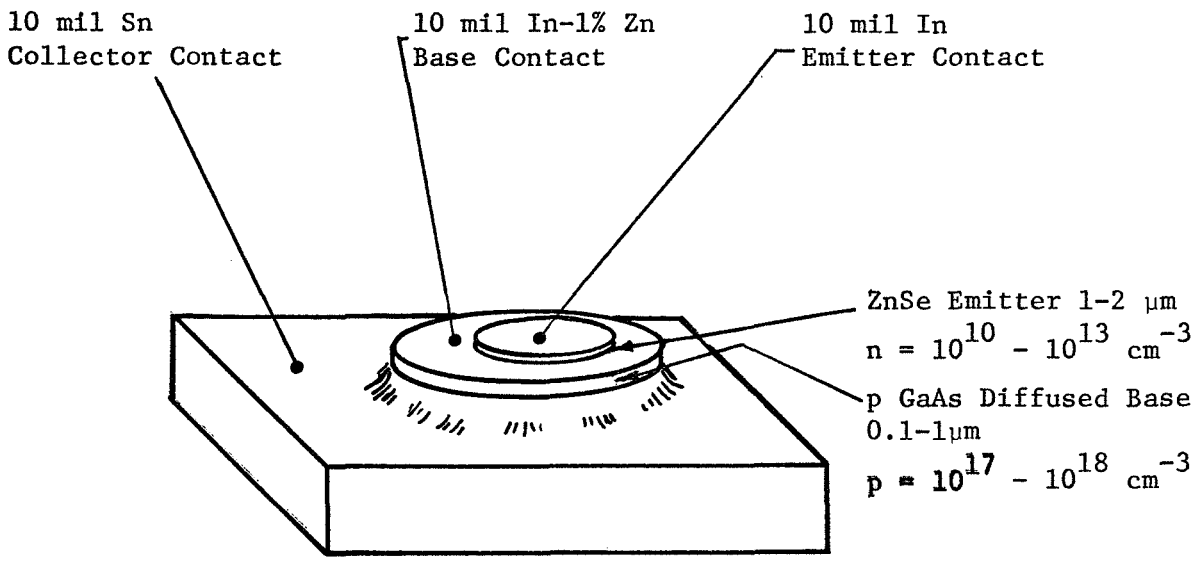


Fig. 2 A typical transistor structure produced by selective etching and alloying metal dots.

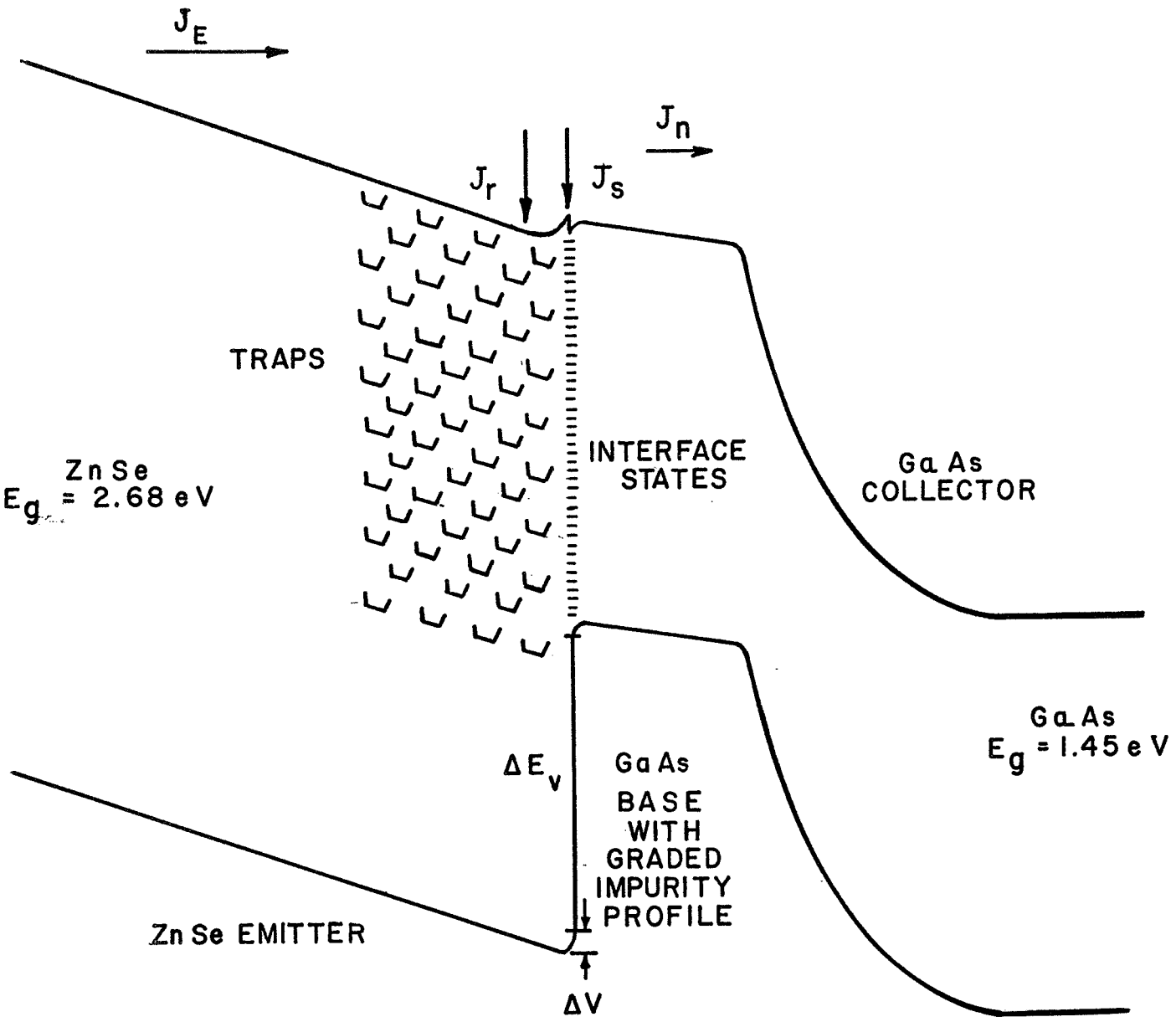


Fig. 3 Energy band diagram of an nZnSe-pGaAs-nGaAs transistor biased for emitter injection and collector collection. The large discontinuity in the valence band, ΔE_v, prevents significant hole injection into the ZnSe. Also shown are the postulated components of emitter current.

provided that the base width and base lifetime are such that significant electron recombination does not occur in the base.

Typical forward emitter-base log I versus V characteristics at 298°K are shown in Fig. 4. The characteristics resemble exponentials, but the change in slope and current magnitude (at any given voltage) with temperature is much less than that theoretically expected. J_s, J_r, or J_n, should depend on the electron concentration at the interface, given by

$$n_{int} = n_o \exp\left(-\frac{q(\Delta V)}{kT}\right) \tag{3}$$

where n_o is the electron concentration at the bulk edge of the ZnSe depletion region, and ΔV is defined in Fig. 3 (Hovel and Milnes 1968). It therefore appears that relatively temperature insensitive space-charge currents in the bulk ZnSe dominate and completely mask out the true junction characteristic. Such behavior was found with ZnSe-Ge devices and is indeed to be expected with ZnSe resistivities of 103 ohm cm (Hovel and Milnes 1968). If the data of Fig. 4 are replotted on log-log scale, the curves in Fig. 5 result. These curves show a high power law region followed by a break into a low power law region. One explanation of the high power law region is the filling of traps in the ZnSe distributed over a wide energy range (Rose 1955, Hovel and Milnes 1968). Although the curves are for ZnSe grown upon (100) oriented GaAs, similar results are obtained for ZnSe on (111)B oriented GaAs.

The reverse emitter-base voltage-current characteristics obey a power law relationship

$$I_{ER} = BV_{BER}^{N} \tag{4}$$

where B depends slightly on temperature but not on voltage and $3.5<N<4.5$. Typically, the reverse current was 10^{-6} amperes at 10 volts reverse voltage.

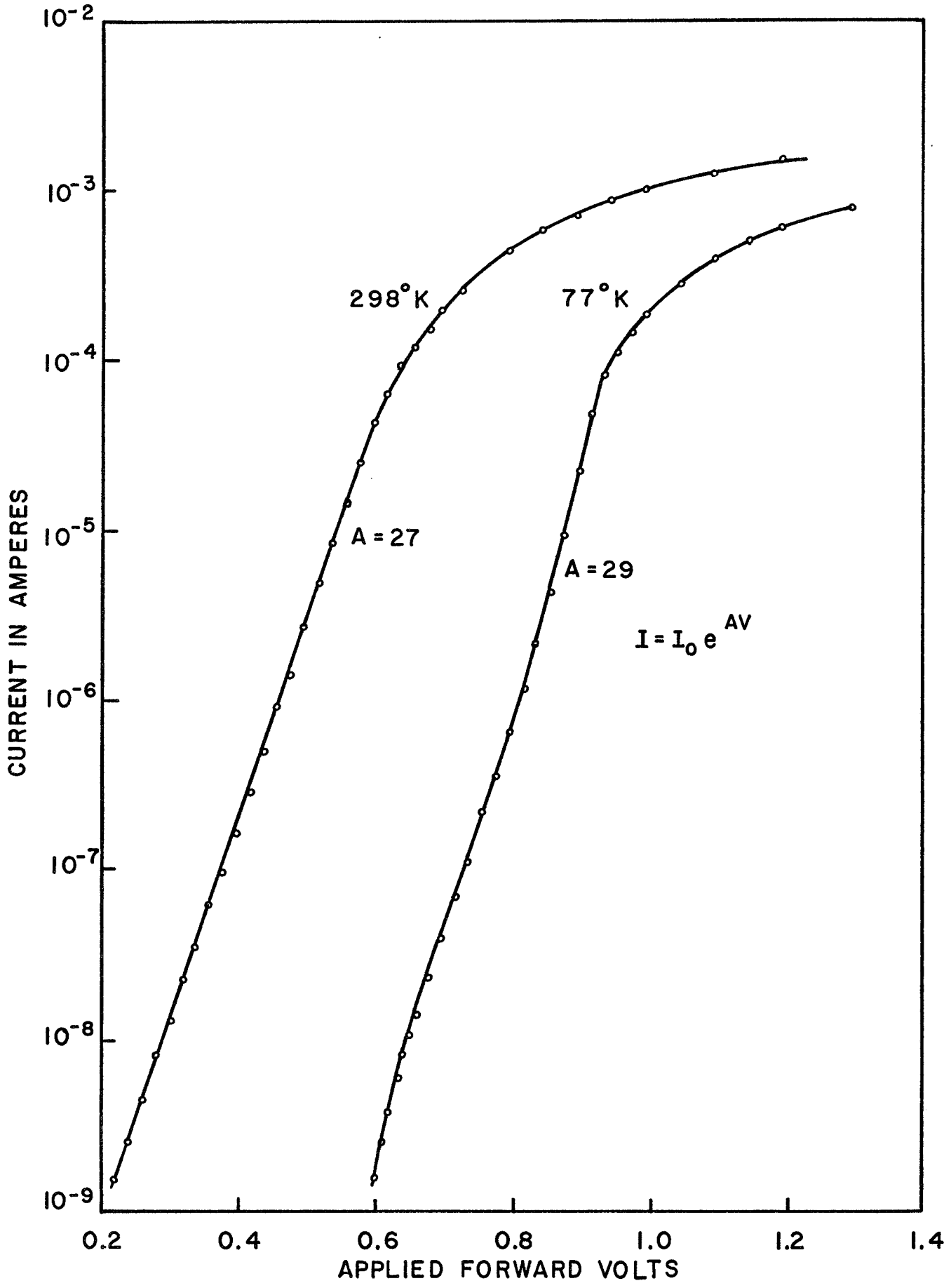


Fig. 4 nZnSe-pGaAs emitter-base characteristics.

The straight line indicates an exponential dependence of current with voltage, but the fact that the slope, A does not change much with temperature suggests a space charge mechanism in the ZnSe (10^3 ohm-cm). The growth was on (100) GaAs, unit TR-13-C-2.

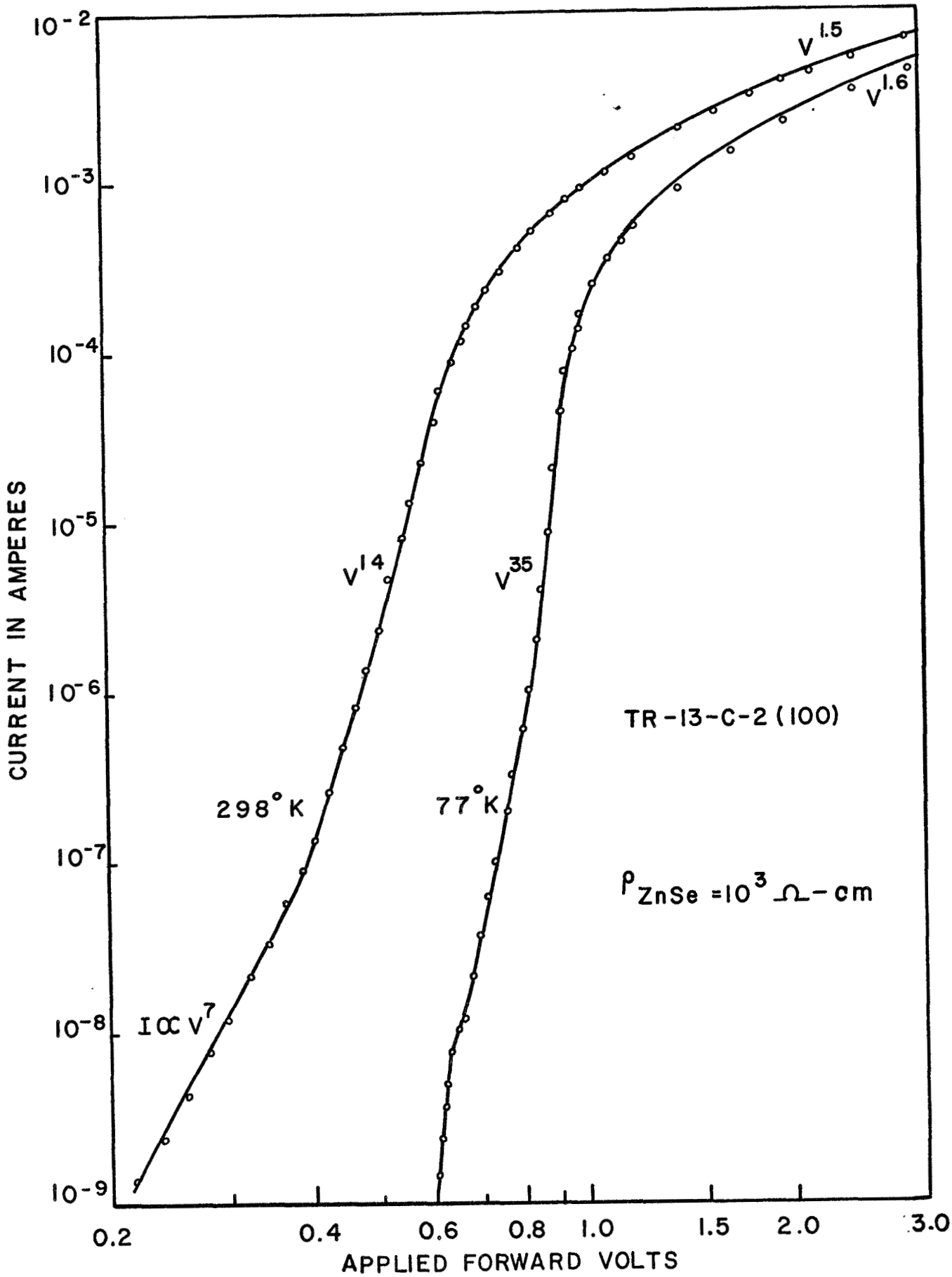


Fig. 5 nZnSe-pGaAs emitter-base characteristics of Fig. 4 replotted on log-log scale.

A high power law dependence followed by a low power law dependence is obtained suggesting space charge flow with considerable trapping action in the ZnSe.

2.3 Transistor Electrical Characteristics

Transistor action in ZnSe-GaAs npn structures provides an indirect means of observing the heterojunction current mechanisms masked by space-charge effects in the emitter-base characteristics.

Experimental results are presented in Figs. 6 and 7 and important physical parameters are listed in Table 1. The effects of these parameters on gain will be discussed.

Table 1

Parameters of Several npn ZnSe-GaAs Transistors

Transistor	GaAs Orientation	Base Width μm	Approx. Base Electric Field At Emitter, Volts/Cm	ZnSe Resistivity Ohm-Cm
TR-5A-1	(111)B	.5	470	10^4
TR-5B-1	(111)B	.2	510	10^5
TR-8A-1	(111)B	.4	510	$5x10^4$
TR-16-C-H	(100)	.3	850	$5x10^5$
TR-17-A-1	(111)B	.4	510	10^4

2.3.1 Injection Level

Typical common-emitter characteristics are shown in Fig. 6 for high and low level injection. The increasing positive slope occurring at the highest injection levels is due to base width modulation effects. Note that the common-emitter current gain, h_{fe} or β, increases with increasing injection level. The variation of gain with emitter current is shown in Fig. 7. Gain increases as a fractional power of the emitter current or is directly proportional to it. Similar behavior has been observed in ZnSe/Ge transistors (Hovel and Milnes 1969b) and explained by considering effects of the defect currents J_r and J_s on gain. The fractional power dependence can be traced to J_r when electrons tunnel through the ZnSe depletion region to reach the interface. The dependence proportional to emitter current may be due to J_s when electron capture dominates

at the interface. The kinks in the lines are probably due to changes in defect mechanisms as emitter current is increased.

2.3.2 Effect of ZnSe Resistivity

ZnSe resistivity effects on gain can be seen in comparing TR-5A-1 and TR-17-A-1 to TR-5B-1 and TR-8A-1 where the ZnSe resistivity is much larger for the last two quoted transistors. Gain is from 5 to 50 times higher (at the same emitter current densities) in higher ZnSe resistivity transistors. A more striking example of this behavior can be seen in the (100) transistor TR-16-C-H which showed absolutely no transistor action with ZnSe resistivity of 10^4 ohm-cm but did show a gain of 2 when the ZnSe resistivity was increased to $5x10^5$ ohm-cm by heating to increase the Zn vacancy-compensation of donors. Higher gain at higher ZnSe resistivities is attributed to a decreasing tunnel component of J_r since the ZnSe depletion layer width increases with increasing ZnSe resistivity (Hovel and Milnes 1969b).

Another effect of the high ZnSe resistivity is a high emitter resistance that dominates the offset voltage and shifts the entire transistor characteristic to the right as seen in Fig. 6. This is an unwanted effect that must be traded-off for gain, in the present state of the heterojunction transistor art with ZnSe.

2.3.3 Base Width and Electric Field Effects

Base width and base electric field at the emitter affect gain. A parameter that is convenient for characterizing these factors is

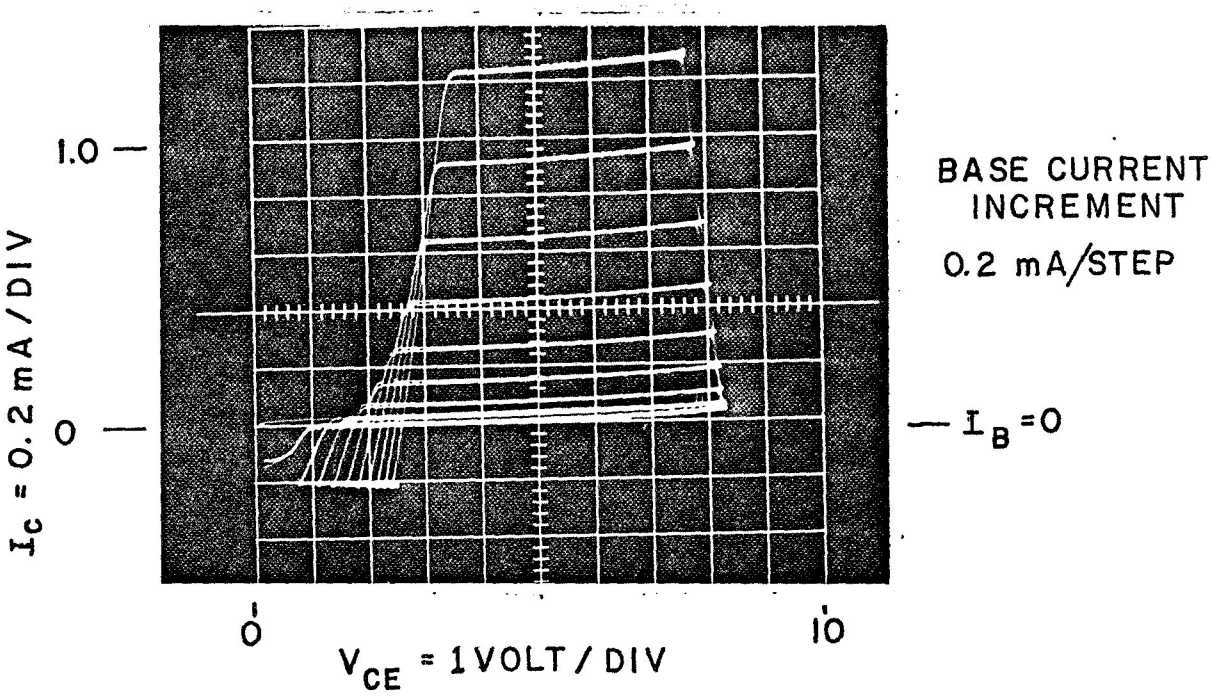
$$\tau = \frac{W}{\mu E} \tag{5}$$

where W is the base width, E is the electric field at the emitter, and μ is the GaAs base mobility near the emitter. For a complimentary error function diffused impurity distribution of Zn atoms in the base, E increases almost linearly by about a factor of 5 in going from emitter to collector so that electrons are field-aided in

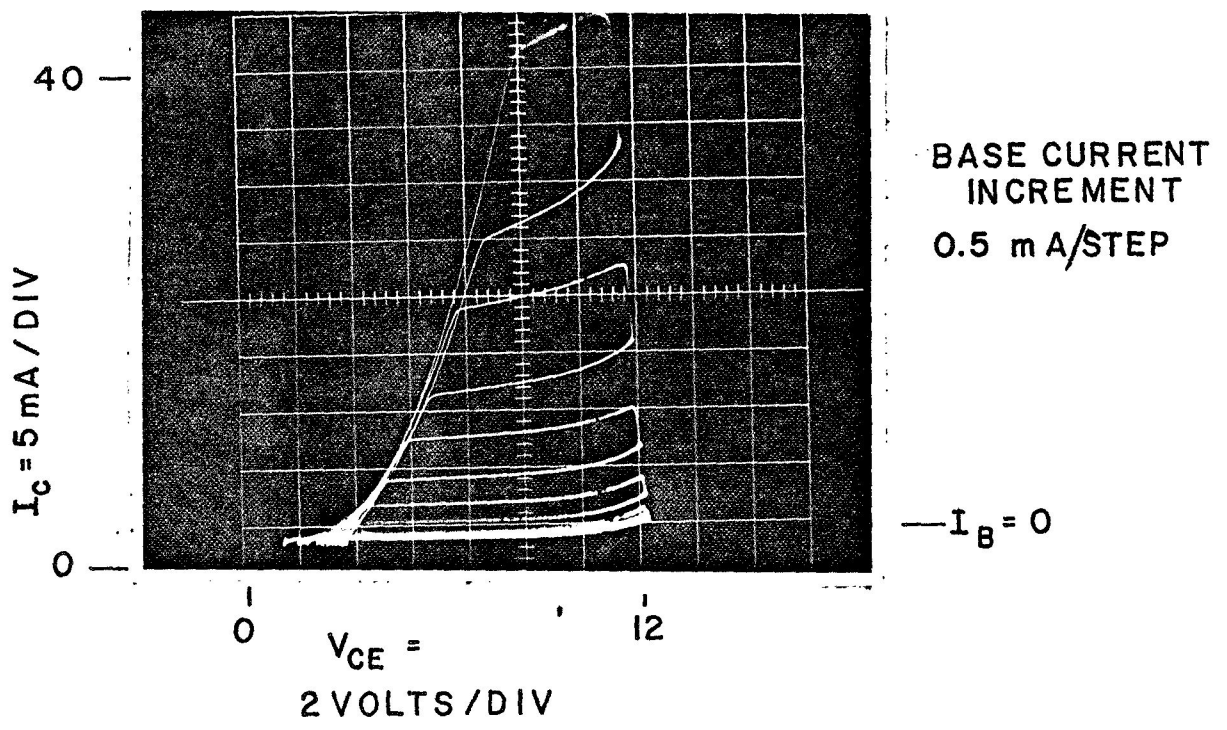
traversing the base. The shorter τ is, the better the base transport factor will be since recombination becomes less probable. It is important to make W as small as possible while making E as large as possible. A typical value of $\tau=2x10^{-11}$ sec. results when W=0.5 μm, E=500 V/cm, and $\mu=5x10^{3}cm^{2}/Vsec$. Enough ZnSe/GaAs devices have not been fabricated to establish fully the effect of τ on gain. However it was found that transistor action ceased (gain goes to zero) when W>0.8 μm. This implies an average base lifetime of $2x10^{-10}$ sec. This does not seem unreasonable since defects and strain introduced by epitaxy can reduce lifetime. As a comparison, lifetimes of 10^{-11} sec are assumed and base-widths of 0.3 μm found necessary to see gain in double diffused npn GaAs homotransistors (Becke et al. 1965).

2.3.4 Orientation Effects

Experimental results indicate that transistor action is strongly influenced by GaAs crystal substrate orientation. Transistors made from (111)B oriented GaAs usually showed gains from 5 to 30 while similarly fabricated (100) oriented transistors showed no gain unless the ZnSe resistivity was made greater than $5x10^{4}$ ohm-cm. The difference in theoretically determined interface states for the two planes due to dangling bonds ($1.45x10^{12}cm^{-3}$ for (111) and $2.51x10^{12}cm^{-3}$ for (100)) does not offer a very plausible explanation for this behavior since the difference is only a $\sqrt{3}$ factor. It could be possible that lifetime in (100) material was much lower than that in (111) material. To test this theory slices of (111) and (100) n-type GaAs were cut from the same boule, polished together, grown upon together, and processed identically into transistors. In all cases the (111) transistors showed gains from 5 to 30 for 0.2-0.75 μm base widths and resistivities of between 10^{3} and 10^{5} ohm-cm. Again (100) transistors showed no gain unless ZnSe resistivity was greater than $5x\ 10^{4}$ ohm-cm. Gains almost independent of emitter current and no larger than 2 were obtained from (100) transistors. Constant gain in these transistors is predicted to be due to interface recombination currents or to



(a) GAIN OF 1 AT I_E = 1.75 mA = 17.5 Amps/cm^2



(b) GAIN OF 30 AT I_E = 46 mA = 460 Amps / cm

Fig. 6 npn ZnSe-GaAs Transistor Common Emitter Characteristics.

The variation of gain with injection level at 298°K is shown.
(Transistor TR-5-A-1 GaAs (111)B)

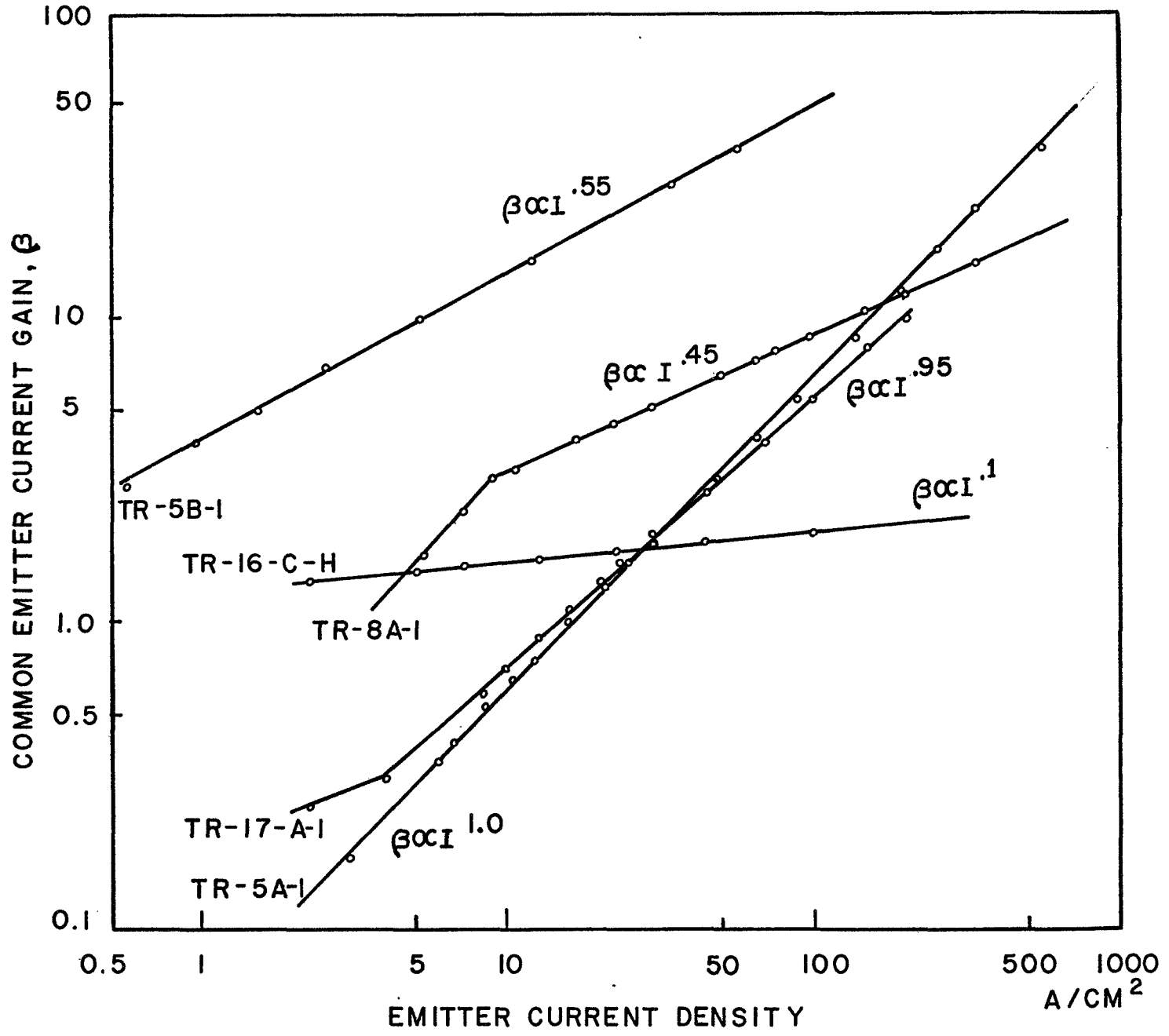


Fig. 7 Variation of gain with injection level, at 298°K.

Note the difference in TR-16-C-H which is (100) oriented - the gain is low and almost current independent.

capture-tunneling currents occurring very near the interface (Hovel and Milnes 1969b). It seems that processes very near the interface are dominating the injection behavior of (100) transistors.

2.4 References

Becke, H., Flatley, D., and Stolnitz, D., 1965, Solid-St. Electron., 8, 255.

Brojdo, S., Riley, T., and Wright, G.T., 1965, Brit. J. Appl. Phys., 16, 133.

Hovel, H.J., and Milnes, A.G., 1968, Int. J. Electron., 25, 201.

Hovel, H.J., and Milnes, A.G., 1969a, J. Electrochem. Soc., 116, 843; 1969b, IEEE Trans. Electron Devices, 16, 766.

Jadus, D.K., and Feucht, D.L., 1969, IEEE Trans. Electron Devices, 16, 102.

Kroemer, H., 1957, Proc. IRE, 45, 1535.

Ladd, G.O. and Feucht, D.L., 1970 IEEE Transactions Electron Devices, in process.

Rose, A., 1955, Phys. Rev., 97, 1538.

Zuleeg, R., 1966, Hughes Research Labs., Contract NAS 12-5.

3. HETEROJUNCTION SOLAR CELL CONSIDERATIONS

In the last quarterly report the results of heterojunction solar cell efficiency calculations were presented.In heterojunction solar cells the output voltage is related to the energy gap of the base semiconductor, namely the material with the smaller of the two

energy gaps. The semiconductor with the larger energy gap acts primarily as a window to photons of energy less than its band gap. The advantage of the heterojunction cell is that this window layer may be proportioned in thickness and doping to minimize the lateral resistance losses in the cell.

The calculated values obtained show that heterojunction solar cells can be hoped for with efficiencies, η_o, comparable to or even greater than the efficiencies obtainable with Si or GaAs homojunction cells. The treatment used, however, neglects junction interface recombination. This is a relatively unknown factor in heterojunction solar cells, since few acceptable structures have been made for study.

The theoretical results with this proviso, show that nZnSe-pGaAs heterojunction solar cells should be capable of greater than 13% efficiency. This compares with about 10.5% for GaAs and 12% for Si homojunction cells, calculated on a similar basis. These values do not include the effects of built-in drift fields on cell performance. In practical Si cells this raises the measured performance to above 13%. A comparable improvement in nZnSe-pGaAs cells might be expected by the provision of a built-in field in the GaAs base region.

The output voltage of a ZnSe-GaAs cell at optimum load power is calculated to be in excess of 0.8 volts and the voltage decline between zero and full load power is 12%. Both of these values are better than for Si homojunction cells, for which the load voltage may be about 0.5 volts and the voltage regulation about 20%. Furthermore the ZnSe-GaAs cell should have an advantage over Si cells in performance at high temperatures, since the energy gap of GaAs is greater than that of Si.

GaP-Si heterojunction cells were also found to be interesting, although the expected efficiencies of about 10.5% are a little lower than for Si cells.

As an alternative to the above, we have also considered an approach in which a hetero-semiconductor face covers a GaAs np homojunction cell. This offers the following features:

(a) The wide band-gap hetero-semiconductor acts as a window that admits photons of energy less than Eg_1. Those of energy between Eg_1 and Eg_2 (1.45 eV) then create carriers in the GaAs homojunction. The wide-gap layer can be quite thick to provide a lower internal cell resistance than can be achieved with homojunction cells. If the layer is several mils thick it may provide inherent radiation resistance.

(b) The lower internal cell resistance made possible by the heteroface contact should allow the adjacent GaAs layer to be redesigned to be more lightly doped and therefore perhaps higher in diffusion length and so a better collector of the photo-induced carriers. The role of the built-in fields in the junction region would also be studied in the course of this redesign.

(c) The nn type interface between the hetero-semiconductor and the GaAs should have a recombination velocity substantially below the value of 10^5 cm sec^{-1} that seems usual for a GaAs surface. This expectation is inferred from the performance of GaP/GaAs and Ge/GaAs junction interfaces as photo-collectors and from the performance of nn abrupt and graded junctions. However direct evidence on nn behavior in GaAs heterojunctions is not very extensive, and the matter would certainly be a question for study.

Reduction of the surface recombination losses below that of conventional GaAs solar cells is however an improvement to be hoped for in this approach. Preliminary calculations suggest that the efficiency of a GaAs homojunction cell would be raised from 10.5% to 15.5% if the surface recombination velocity could be decreased from 10^5 cm/sec to 10^3 cm/sec. However, if this surface recombination velocity control is obtained by providing a hetero-semiconductor face of GaN or GaP as the wide-gap semiconductor, then the obtainable efficiency reduces from 15.5% to 15% or 13%, respectively, by absorption loss in the window material.

(d) When the heterojunction itself is nn or pp, its electrical performance is not as critical as it would be if it formed the np junction, on which the solar cell collection efficiency hinges. A recent example of the use of a heterojunction as a pp structure is that found in nGaAs-pGaAs-p$Al_{.5}Ga_{.5}As$ injection lasers. Here the heterojunction brings about a confinement action that has greatly improved the 300°K threshold current density of such lasers.

For the hetero-semiconductor studies a wide band-gap material is required with good doping and contact technology, and preferably a lattice and expansion-coefficient match to GaAs. There are a number of possibilities e.g. GaN, AlGaAs, GaP etc., that we believe should be explored.

4. LOW TEMPERATURE GROWTH OF GeON GaAs BY IODINE TRANSPORT

During the quarter we continued our studies of iodine transport of Ge to fabricate pGe-nGaAs structures.

The series of p-type Ge growths made at 400°C using the inverting seed holder and reported earlier were diced after lapping off a small amount of Ge which grew on the rear of the slice. These dice were then masked and etched, and dots alloyed into both the exposed GaAs surface and into the Ge mesas. As had been done previously, a tungsten probe contact directly to the mesa was used to pass current through the device and a probe contact to the mesa alloy dot was used as a potential probe. A probe contact to the GaAs alloy dot served as return for both the current and potential probes. Devices from one run (H123) showed a near ohmic character in all of several diodes made on different dice and were therefore eliminated. Devices from two other runs showed good probe-plotted V-I characteristics at room temperature. These two, along with device H113-1 which had previously shown a room temperature value η=1.1, were probe plotted at dry ice temperature and H113-1 at liquid nitrogen temperature as well. The η values obtained are given in the table below.

Table 2

η Values of Several p-Ge/n-GaAs Heterodiodes

	Probed Chip Device			Header Mounted Device		
Device	300°K	194°K	77°K	300°K	194°K	77°K
H113-1	1.1	1.4	3.3	1.8	3.2	4.3
H124-2	1.3	3.2	-	1.5	4.6	-
H125-3	1.0	2.5	-	1.1	3.5	12

While the values of η at room temperature are near unity, the linear portions of curves plotted at different temperatures on semi-log paper are nearly parallel. This latter piece of evidence would tend to indicate that the observed current is not due only to carriers being excited over a potential barrier.

All devices had an excessive amount of series resistance, even at room temperature. They were therefore mounted on headers with a second contact alloyed to the germanium mesa and a large area contact to the rear of the GaAs substrate. Measurements were made on these devices using the new contacts to make two current contacts and a separate set of two potential contacts. These measurements yielded η values which were considerably poorer than those obtained from unmounted devices. The slope of these new characteristics varies considerably with decreasing temperature in an unsystematic manner.

The initial suspected source of this degradation was surface contamination of the junction resulting from processing operations in mounting. An attempt was made to clean up these junction surfaces by wax masking and chemical etching. However, the only change in the characteristics observed was a reduction in currents proportional to the mesa area etched with no resulting change in current density. In order to improve interface cleanliness and junction characteristics, growths are now being made on freshly cleaved GaAs seeds. Should this not significantly improve the junctions, an apparatus is planned to allow cleaving of the GaAs in situ after germanium deposition has begun.

5. PUBLICATIONS AND PAPERS PENDING

A research note "ZnTe-InAs Heterojunctions" was published in Int. J. Electronics (1969 Vol. 27, No. 4, 383-386) during the quarter.

Accepted this quarter for publication: "Heterojunction Solar Cell Calculations", Solid State Electronics. Also due to appear, as stated in the last quarterly report, are papers entitled: "Autodoping Effects at the Interface of GaAs-Ge Heterojunctions", AIME Transactions of the Metallurgical Society; "Performance Potential of High Frequency Heterojunction Transistors", IEEE Transactions on Electron Devices.

6. CONTRIBUTORS

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