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PROGRESS REPORT ON GaP,
GROWN JUNCTION, HIGH TEMPERATURE DIODES

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by

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Abstract

This memo discusses current results of an effort to develop GaP (Gallium Phosphide) diodes for high temperature, $> 275^{\circ}\text{C}$, applications. It discusses the theory, fabrication and testing of devices made at Sandia National Laboratories.

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I. Introduction

Geothermal, in situ coal gasification and other new energy sources require high temperature (275°C and higher) semiconductor devices for probing and monitoring applications. This memo describes some recent work on Gallium Phosphide (GaP) diodes being developed to meet these needs.

II. Theory

The choice of semiconductor material used to fabricate diodes is dominated by the reverse leakage characteristics desired. The reverse leakage current density of an abrupt p⁺-n junction is given by:^{1,2}

$$J_R = e \sqrt{\frac{D_p}{\tau_p}} \frac{n_i^2}{N_D} + \frac{e n_i W}{2 \tau_o} \quad (1)$$

where D_p = hole diffusion coefficient

τ_p = hole lifetime (in the n region)

τ_o = depletion region carrier lifetime

n_i = intrinsic carrier concentration

e = electronic charge

N_D = donor concentration

W = depletion layer width

The first term on the right side of Eq. (1) represents the diffusion of minority carriers within a diffusion length of the junction which produces a reverse leakage current. This component is independent of bias. The second term on the right side of Eq. (1) represents generation-recombination current in the depletion region and is dependent on bias through the depletion

width. Generally the recombination current term will dominate at low temperature and the diffusion current term will dominate at higher temperatures. The cross over point is primarily dependent on the semiconductor band gap and carrier lifetime. The appropriate parameters for Silicon (Si), Gallium Arsenide (GaAs) and Gallium Phosphide (GaP) are given in Table 1. These materials are of interest because of their state of development and availability.

Table 1 Material Parameters

Material	N_D cm^{-3}	D_p $\text{cm}^2 \text{s}^{-1}$	τ_p s	τ_o s	W microns @-3V	E_g eV	N_o cm^{-3}
Si	5×10^{15}	15	10^{-6}	10^{-6}	1.0	1.12	10^{16}
GaAs	6×10^{15}	10	10^{-9}	10^{-9}	0.9	1.43	2.9×10^{15}
GaP	1.5×10^{16}	1.9	10^{-7}	10^{-7}	0.6	2.24	10^{16}

These doping levels should produce an abrupt P^+-N junction reverse breakdown of 100V. The intrinsic concentration, n_i has the following form:

$$n_i \cong N_o T^{3/2} \exp(-E_g/2kT) \quad (2)$$

Using Eq.(2) and Table 1, Eq.(1) can be evaluated as a function of temperature for the three materials. This was done assuming that the parameters in Table 1 are independent of temperature. While this is not strictly true, the exponential temperature dependence of n_i should overshadow the smaller variations of D_p , τ_o and τ_p .

The results for reverse leakage current density at -3V are shown in Figure 1. The arrows on the curves mark the crossover temperature of the two components of leakage current. For temperatures to the left of the arrows generation-recombination current dominates and diffusion current dominates at temperatures to the right.

The figure shows that for temperatures in the 20-300°C range GaAs and Si have similar leakage currents. (The high depletion region generation-recombination current in GaAs offsets its wider bandgap.) At higher temperatures, GaAs has about an order of magnitude less leakage current than Si. Calculations show that GaP diode reverse leakage should be dominated by generation-recombination current up to 650°C and is at least 5 orders of magnitude lower than Si. Hence it can be seen that GaP should be an excellent choice for high temperature semiconductor devices.

This fact is demonstrated in Figure 2. This figure shows a planar epitaxial, P^+-N , Si diode (Fairchild FD300) compared to a Sandia made P^+-N GaP diode both at 20°C and 400°C. The Si diode is very leaky at 400°C and the leakage of the GaP diode is not discernable on the curve tracer. The measured current densities at -3V and 400°C are 57 amp/cm² for the Si diode and 7×10^{-4} amp/cm² for the GaP diode. These data points are also plotted on Figure 1.

The remainder of this memo discusses the fabrication and evaluation of the Sandia grown junction GaP diodes.

ABRUPT P⁺-N DIODES

Figure 1. Comparison of reverse leakage current density vs temperature for GaAs, Si and GaP

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● Silicon 20°C ↑

● Gallium-Phosphide 20°C ↑

● Silicon 400°C ↑

● Gallium-Phosphide 400°C ↑

● (Horizontal Scale = 5V/div, Vertical = 1 mA/div)

Figure 2. Comparison of Si epitaxial and GaP grown junction diodes.

II. Diode Structure

The diode structures used are grown junctions fabricated by L. R. Dawson (5154). The abrupt P^+ -N junctions were prepared by liquid phase epitaxial growth of the P^+ and N layers on an N^+ substrate during a single growth run. This technique was not possible until the development of a growth technique using the low vapor pressure magnesium dopant by Dawson.³ The wafer was metallized and cut into dice and packaged in the 5100 processing lab by J. B. Snelling (5133). A sketch of the diode is shown in Figure 3. The diode metallization system used was:

P^+ contact - Be/Au ($3000 \text{ \AA} \sim 1\% \text{ Be by weight}$)

(7 mil dot) followed by $3000 \text{ \AA}$ of pure Au (vacuum evaporated)

N^+ contact - The contact was sputtered (full surface) in the following sequence:

Au/Ge (88/12) $\sim 1000 \text{ \AA}$

Au $\sim 250 \text{ \AA}$

Ni $\sim 600 \text{ \AA}$

Au $\sim 4000 \text{ \AA}$

Contacts annealed 450°C (10 minutes) in H_2

The first lot of diodes tested were mounted in ceramic flat pack headers (N^+ side down) with a high temperature, polyimide silver loaded 71-1 epoxy (from Ablestick Labs, Gardena, CA). Gold wires (1.5 mil) were used to make contact to the top of the die. Figure 4 shows photographs of the finished devices.

Figure 3. Grown Junction GaP Diode.

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A. GaP Diodes - Close-up View

B. Diodes - Packaged on Header

High Temperature Life Test GaP Diodes

Figure 4. Silver epoxy mounted GaP diodes (after life test).

III. Diode Characteristics

A typical I-V characteristic of a GaP diode was shown in Figure 2. Figure 5 shows a detailed reverse I-V curve taken at 400°C. The breakdown characteristic remains fairly sharp even at this elevated temperature. The fact that the leakage current is larger than the value predicted in Figure 1 means that there is some leakage at the sawed edges of the die. This is further supported by the fact that the dependence of the reverse current on voltage is linear (see dashed line - Figure 5). Normal generation-recombination current should vary with the square root dependence expected of the depletion width, i.e.:

$$W = \sqrt{\frac{2\epsilon_s (V_{bi} + V_R)}{eN_D}} \quad (3)$$

where $\epsilon_s = 8.85 \times 10^{-13} \text{ F cm}^{-1}$,
 $V_{bi} = 2.2\text{V}$ (for GaP),
 $V_R = \text{applied reverse bias.}$

The zero bias capacitance of the 15 mil square chips was measured to be 22 pF. This corresponds to a 0.56μ zero bias depletion width (close to the 0.4μ value predicted by Eq. 3).

Figure 5. Reverse I-V characteristic of GaP diode at 400°C.

IV Environmental Tests

The GaP diodes were subjected to a life test under bias by T. A. Plut (org 5133). Three bias conditions were used; forward bias, reverse bias and open circuit (zero bias). The circuits used are shown below in Figure 6.

Figure 6. Environmental Test Circuits

The diodes were mounted on headers as shown previously in Figure 4. The headers were placed in ovens at 300°C. The headers were not sealed and the oven contained room air. The parameters of the diodes were checked as a function of time in the oven. Forward and reverse I-V data were taken using the circuits shown in Figure 7.

Figure 7. Data Acquisition Circuits

The tests on the silver epoxy bonded diodes (Figure 4) were as follows:

- 1) 9 diodes @ 50 mA, FB in 300°C air
- 2) 9 diodes @ -10V, RB in 300°C air
- 3) 9 diodes @ 0V, OB in 300°C air

One of the oven temperature controllers failed on the first day, destroying the forward bias samples at 800°C. To replace these, 9 more devices from the same lot were mounted and life tested. Detailed internal reports on these tests were written (Ref. 4,5). The basic finding was a dramatic increase in forward voltage drop (increase in series resistance) of the diodes biased at -10V RB. A small but noticeable degradation in series resistance was also seen in those diodes held at OB and FB. C-V profiles of aged and unaged devices showed no substantial change in carrier concentration adjacent to the p-n junction. Figure 8 shows the average of the data for the silver epoxy bonded diodes. The figure shows a large increase in series resistance occurring at about 400 hours.

A close inspection of the diodes showed that the silver migration out of the organic epoxy binder was the cause for the increased series resistance. Figure 9 shows close-up views of both the zero bias and reverse biased diodes after 1128 hours at 300°C. The initial epoxy bond was a small dot almost the same size as the die. Figure 9A shows a large diffuse ring around each of the die. This is silver which has migrated out of the epoxy and resulted in a poor connection (high resistance) to the die. Figure 9B shows a similar view of the diodes held at zero bias and 300°C for 1128 hours. The silver diffusion rings are much smaller in this case and there is still enough silver left in the epoxy binder to make a low series resistance connection to the diode. This explains the data shown in Figure 8. The cause of the accelerated silver migration at reverse bias is not known at this time. Rather than pursue this problem it was decided to stop using this epoxy.

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High Temperature Diode Life Test

Figure 8. 300°C Life Test Data on Silver Epoxy Bonded GaP Diodes.

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A. Diodes After 1128 Hours at Reverse Bias (300°C)

B. Diodes After 1128 Hours at Zero Bias (300°C)

Figure 9. (A) Silver diffusion ring for reverse bias,
(B) Smaller ring at zero bias.

A second lot of diodes was fabricated from the same wafer. These diodes were the same size and came from the same metalization run as the first devices. These diodes were mounted in a stress free configuration using 1.5 mil diameter gold wires bonded to each side of the chip. This was done to eliminate any die attach stresses or material interactions due to the header attachment scheme. These devices are shown in Figure 10. It should be emphasized that the mounting configuration shown in Figure 10 is not proposed for fielded devices, but rather it is a scheme used to remove any contribution of header stress or bonding agent reactions. The test plan used for these diodes was:

- 1) 3 diodes @ 5 mA FB in 300°C air.
- 2) 9 diodes @ -10V RB in 300°C air.
- 3) 3 diodes @ 0V OB in 300°C air.

The forward bias level was reduced from that of the previous test due to the lack of heat sinking in the free mounted diodes. The diodes were placed, unsealed, in ovens at 300°C and biased using the circuits shown in Figure 6. Data were taken as function of time using the circuits shown in Figure 7. The details of this test were documented in an internal memo (Ref. 5). The results of this test are summarized in Figure 11. This figure shows that no detectable degradation in series resistance occurred in any of the three bias states. The room temperature reverse leakage did show a slight increase, increasing from nominally 10^{-9} amps to 10^{-8} amps after 991 hours at 300°C. There was not a strong correlation between bias state and leakage increase. The reverse leakage at 300°C showed a slight decrease after 991 hours. This stability in diode parameters is interpreted as meaning that the diode metallizations and junction dopants are stable at 300°C with bias for at least 1000 hours.

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A. Packaged Diodes (3)

Figure 10. B. Diode Close-Up View

STRESS FREE GaP DIODE LIFE TEST (300°C)

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High Temperature Diode Life Test

Figure 11. 300°C Life Test Data on Stress Free GaP Diodes.

V. N⁺ Contact Study

During the first life test the observation was made that the reverse biased diodes were degrading much faster than zero biased, or forward biased devices. Previous studies (Ref. 7) on GaAs diodes had also experienced a similar effect and attributed it to the substrate-header interface. Ohmic contacts were made on GaP N⁺ and P⁺ substrates to evaluate possible degradation of the contacts and to determine if the degradation would be bias sensitive. Ohmic contacts were formed in sets of three (triads) on the substrates as shown in Figure 12. These contacts used the same N⁺ and P⁺ metallization scheme described in Section II of this report and hence were identical to backside and frontside contacts used on the GaP diodes. The substrates were mounted in flat pack headers and aged at 300°C. During the aging a continuous current was passed between two of the contacts in each triad, the third contact was left unbiased. Periodically the bias was disconnected and the two biased contacts were probed by measuring the resistance between the unbiased contact and each of the biased contacts in the triad. The purpose was to find out if the contact aging would be sensitive to the direction of current flow through the contact. The results of this test were totally negative, i.e., no degradation of contact resistance was seen with temperature and bias. This result was interpreted to mean that the N⁺ and P⁺ contact scheme described in Section II is stable at 300°C under bias. This result is in agreement with the absence of degradation in the tests of the "stress free" devices described previously.

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Figure 12. GaP N^+ Substrate Contact Degradation
Test of Au-Ge Contacts (300°C Test)

VI. Plans and Recommendations

The tests to date have shown that the GaP basic junction and ohmic contacts are stable at 300°C and bias for 1000 hours. The mounting scheme shown in Figure 10 is not, however, mechanically rugged enough for field application and does not offer any heat sinking for the diodes. The future effort will be directed at developing a non degrading die attach system for bonding the diodes to the headers. A Ge/Au eutetic may be a good choice. During the "stress free" life test we included a single diode mounted to the header using a Ge/Au preform. This device also showed no increase in series resistance. Therefore, we plan to fabricate and life test another group of GaP diodes using this bonding system.

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