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IMPROVING THE EFFICIENCY OF GaP LED'S WHICH EMIT GREEN LIGHT

BY
I. LADANY AND H. KRESSEL

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16. Abstract

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SUMMARY

A study of techniques for preparing n-type material and junctions which yield the most consistent high diode-efficiency values has high-lighted the role that Ga vacancies and/or associated defects play in reducing the green luminescent efficiency of n-type GaP. A useful method for obtaining good quality material has been developed. It has been shown that junction formation at high temperatures in a process where the n to p transition occurs without removing the substrate from the furnace yields devices superior to those obtained by diffusion or double epitaxy in the conventional manner previously used for GaP junction formation.

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The efficiencies of structures containing (AlGa)P-GaP heterojunctions were investigated. The results were disappointing in all cases in that the efficiency was lower than in homojunctions.

Both Be and Mg have been studied as possible substitutes for Zn. There appears to be no obvious advantage to their use at this time although the reduced red emission at room temperature obtained when Mg is used may have special applications.

Various structures have been studied for numeric displays. A monolithic green GaP numeric element has been made for the first time by Zn diffusion. Segmented displays have also been made with an estimated brightness of 400 fL at a drive current of 20 mA per segment having a length of 1.1 mm and a width of 0.3 mm.

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I. INTRODUCTION

The near-bandgap radiation of GaP which peaks at about 5600 Å, is very close to the wavelength of maximum eye response (Figure 1). This makes GaP potentially the most useful of all visible semiconductor light sources. Research on these electroluminescent

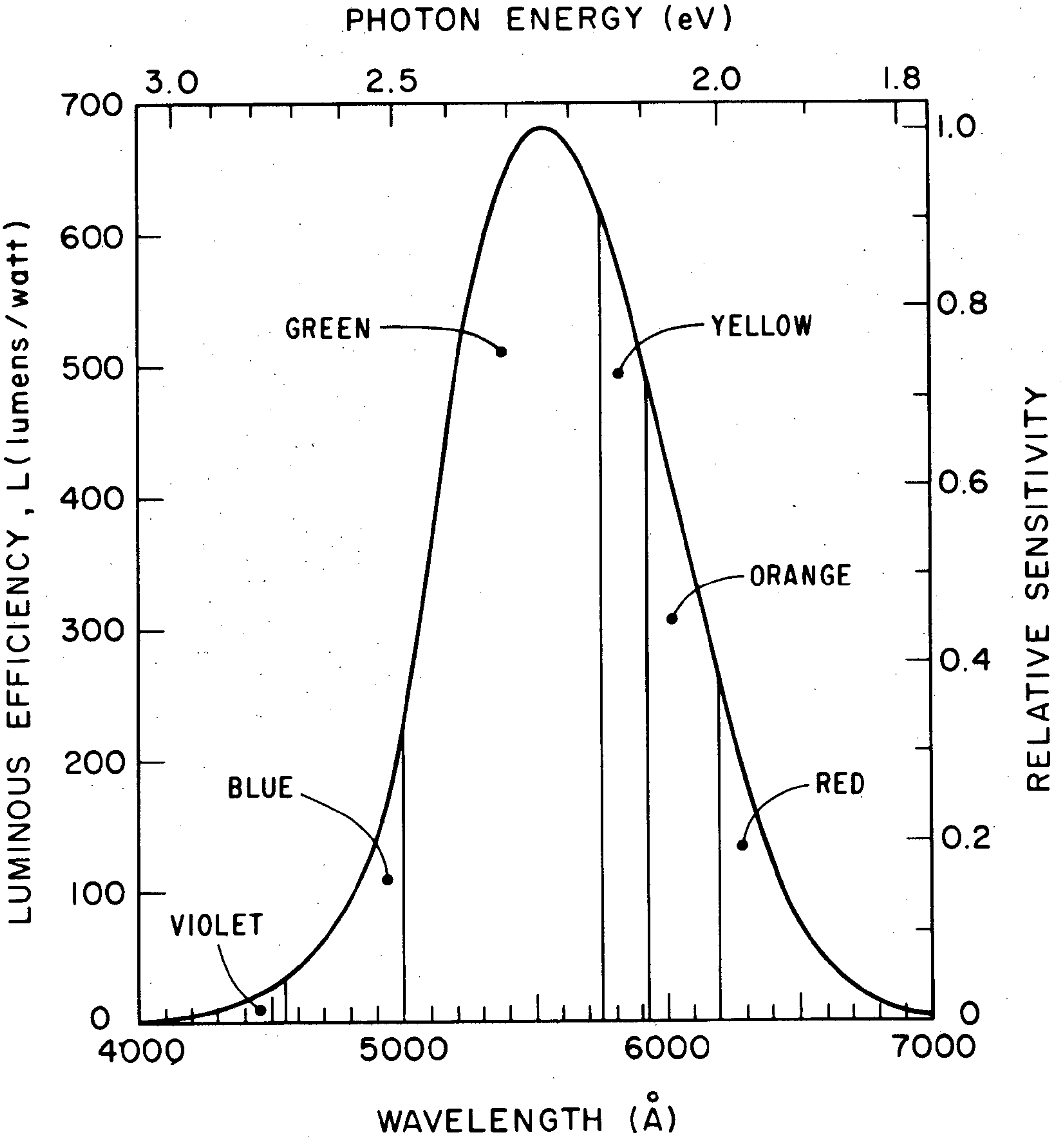

Figure 1. Relative sensitivity of the eye.

diodes began over a decade ago, but efficient green emission has only been obtained since the development of the liquid-phase epitaxial technique and the discovery that nitrogen enhances the near-bandgap radiation at room temperature. The recent development of techniques for growing large-area single crystals in ingot form from the melt has been an additional factor in increasing the interest in GaP diodes for practical systems.

Despite the extensive prior research on GaP materials, however, it has proved difficult to reproduce high efficiency green-emitting LEDs for reasons which were poorly understood. The objectives of the present program were to investigate the key factors believed to be most relevant in determining the efficiency of these diodes and to develop processes for their fabrication. These objectives have been achieved. We have studied diodes made by diffusion and multiple epitaxial growth under a variety of liquid-phase synthesis conditions. On the basis of this work, a new process involving double epitaxy has been developed which yields double epitaxial diode efficiencies as high as 0.7%, which is superior to values previously reported. In addition, a technology has been developed for assembling these diodes into useful configurations, including a numeric display.

II. BASIC MATERIALS AND DEVICE PROPERTIES

A. Preparation and Properties of n-Type Material

It is well established that N is needed to obtain the highest possible room-temperature green-emission efficiency (Ref. 1), but the correlation between the nitrogen concentration in the solid and the efficiency is not easily established because: (a) some N is always present in the material (even without its addition to the growth solution), (b) it is difficult to measure the N concentration in the important regions of the diode, and (c) other factors which can depress the diode efficiency can mask the effect of nitrogen.

Some major factors which can degrade the diode efficiency are: (1) vacancies and associated impurity complexes which in GaAs are known to be nonradiative centers (Ref. 2) and can be expected to behave similarly in GaP, (2) contaminants such as Cu, and (3) defects at the p-n junction interface (dislocations and associated precipitates) which result from the lattice parameter mismatch due to difference in the impurity concentration.*

Thus, despite the fact that the radiative efficiency of the material as measured by photoluminescence in the *bulk* of the n-side of the junction is high, the diode efficiency can be low because nonradiative recombination can occur in the p-n junction interface region. This is particularly significant in GaP because the minority-carrier diffusion length is so short--0.2 to 0.5 μm (Ref. 4) that the bulk of the carriers actually recombine very near the p-n interface.

While the p-side of the junction may contribute to the green emission at room temperature, microscopic examination of forward biased diodes, as well as a comparison of the photoluminescence (PL) from the n-side of the junction and electroluminescence (EL) suggest that much of the green recombination occurs in the lightly doped n-side of the junction in the devices of interest here.** Figure 2 shows a comparison of the diode El and PL from the n-side layer of the kind used in our diodes. While the major features are similar, note that the high energy side of

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*X-ray topographs have indeed shown that such dislocations exist (Ref. 3).

**In any case, the Zn diffusion during and after growth places the junction into what was originally the n-type layer.

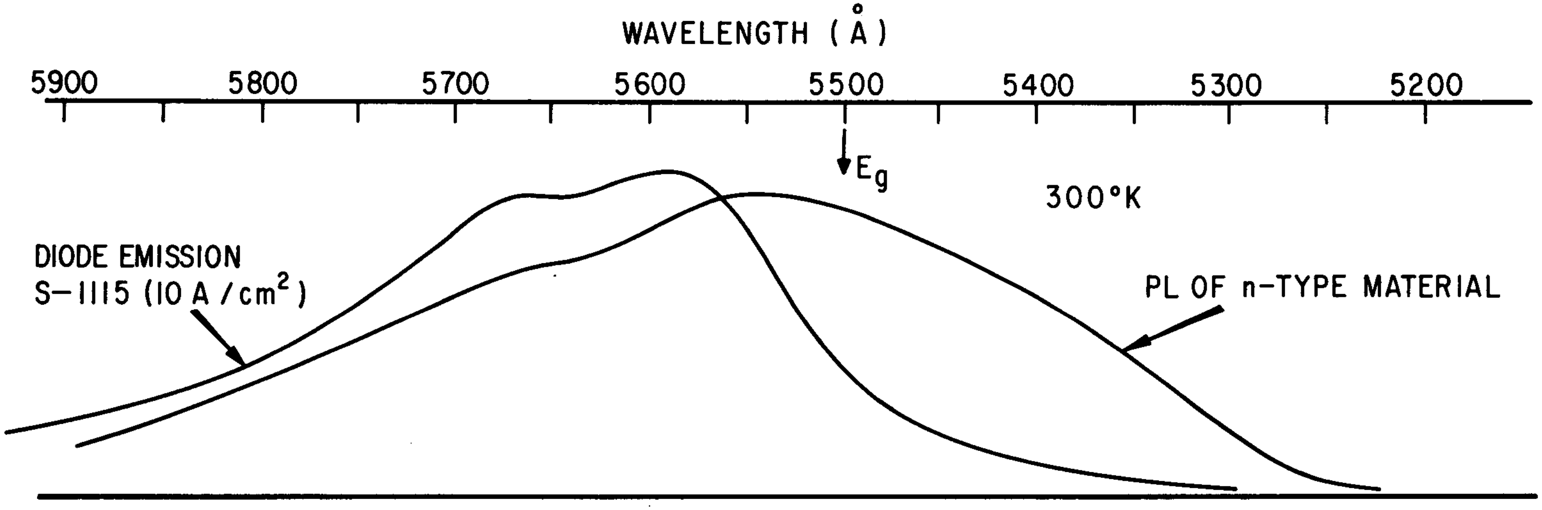


Figure 2. PL of a high-efficiency n-layer and EL from a diode grown on that layer.

the emission is reduced in the EL spectra because of selective internal absorption in the diode. The PL spectra have been extensively described in the literature (Ref. 1), and we will only note some of the key features. The relative magnitude of the 5540 Å line and the 5650 Å line depends on the nitrogen concentration in the solid with the intensity of the 5650 Å line increasing with N concentration. It should be noted that in the presence of a high N content, the emission of the diode is no longer purely green but is closer to yellow.

In addition to the green emission, the spectra include some red emission at room temperature, which is not usually identical for the n-type PL and the EL. In the diodes the red EL band is centered at about 6900 Å and is identical to the Zn-O pair recombination band. It is due to residual oxygen in the grown material. The PL band of the n-type material, on the other hand, is broader and shifted further into the infrared, being centered at ∿ 7200 Å. This band is attributed to a complex center associated with Ga vacancies. The relative PL intensity of the 7200 Å red band compared to the green band at 300°K was found to qualitatively correlate with the efficiency of the diodes made in that material. The diodes made from n-type material with the highest PL ratio of green-to red intensity at 300°K are generally the most efficient ones. This ratio varies with the method of preparing the n-type material. We have prepared n-type layers on large-area melt-grown "liquid-encapsulated" (LEC) substrates. Among the key variables in these experiments were the nitrogen concentrations and the growth technique. Two major growth methods were used: Group I material was grown in a "quasi" sealed crucible, while group II material was grown under flowing hydrogen in an open-tube system.

The "quasi" sealed crucible is shown in Figure 3. It consists of a vitreous carbon boat inside an Al_2O_3 tube fitted with an Al_2O_3 plug. The crucible can be manipulated from outside the furnace thus allowing the atmosphere surrounding the solution and wafer to be controlled. In the open-tube method for Group II material, a conventional tipping furnace was used with a boat containing a vitreous carbon liner. Palladium diffused hydrogen is continously flowed over the solution at ≈ 50 cm^3/min.

The PL characteristics of Group I and Group II material differed significantly. Group I material showed low relative PL efficiency at room temperature with mostly long wavelength emission, while Group II material showed much higher efficiency with the emission concentrated in the green. The EL obtained from a

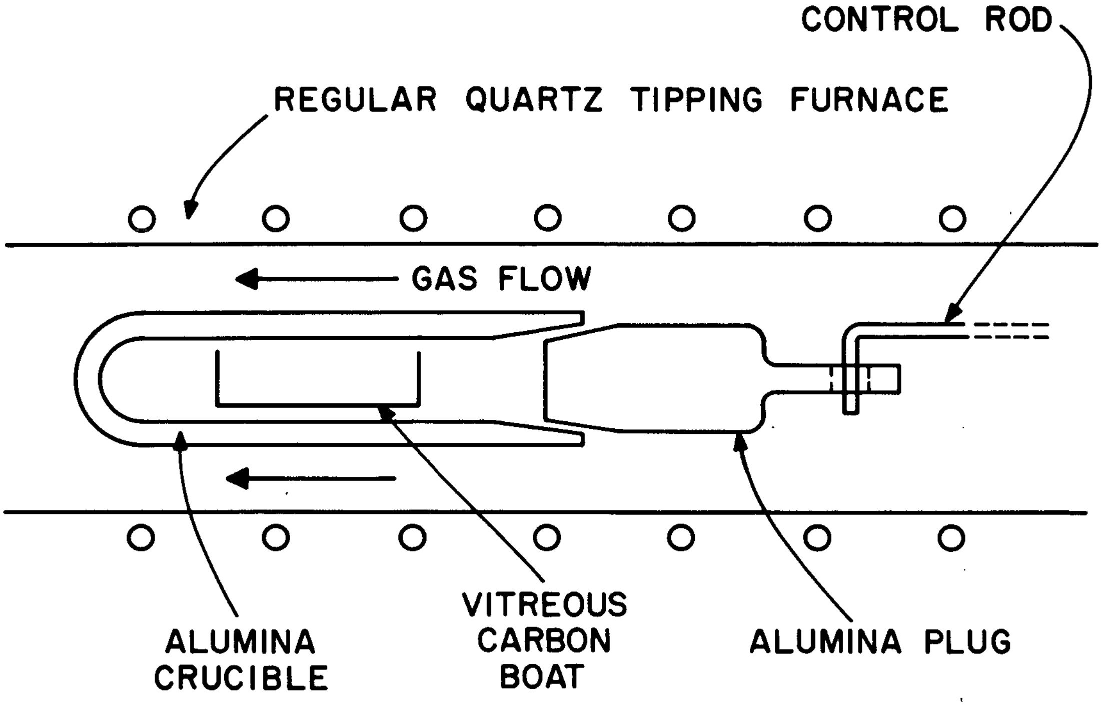


Figure 3. Quasi-sealed crucible.

diode where a p-layer is grown on Group I material (Figure 4) shows very weak green emission with the red emission dominating. The opposite is true with diodes made from Group II material.

Inefficient n-type layers similar to Group I material were also obtained by growing in a stagnant atmosphere in the furnace by restricting the flow of hydrogen in the furnace during growth. The similarities in the results obtained are attributed to the fact that in both cases the predominant vapor species (phosphorus) is kept at a higher level than under flowing hydrogen conditions. At the growth temperature, the partial pressure due to P_2 (and P_4) is larger than the partial pressure due to Ga. Thus GaP decomposes to give P_2 (or P_4) in the vapor (Ref. 5) which affects the Ga vacancy concentration in the solid, $C_{V_{Ga}}$, since

$$C_{V_{Ga}} \propto \left[P_{P_2}\right]^{1/2} \tag{1}$$

In a stagnant atmosphere or in a sealed crucible, where the pressure P_2 increases, more Ga vacancies are generated than in a stream of H_2 where the P_2 is swept away.

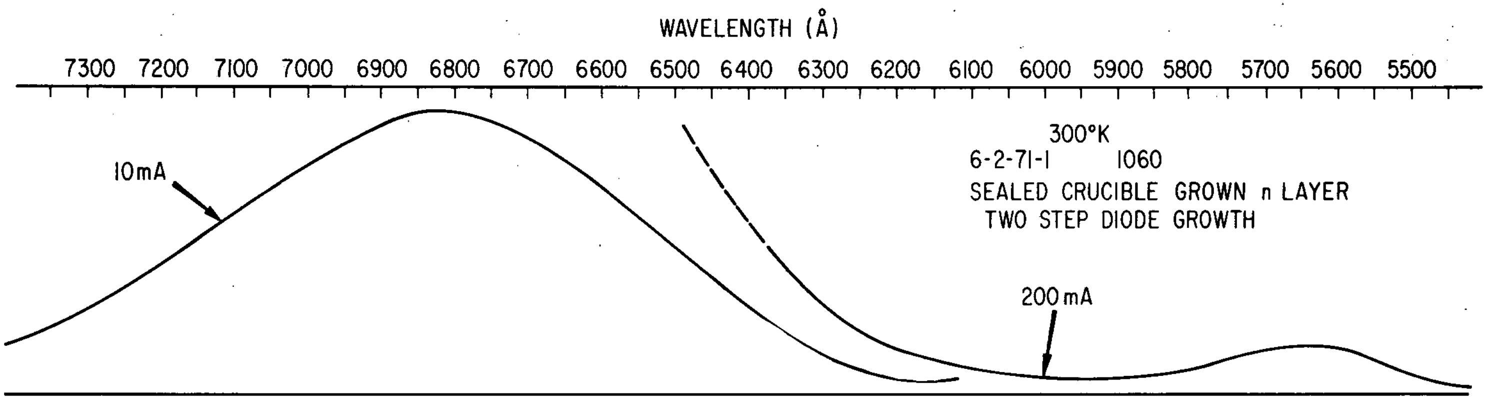


Figure 4. EL of two-step diode from n-layer grown in sealed crucible. The spectra are not corrected for the S-20 photoresponse.

We have tested this model by another experiment where the P_2 pressure was reduced. A nitrogen-doped layer was grown in a sealed crucible as before, but one end also held a reservoir of Ga to trap the phosphorus vapor. At the end of the run, GaP platelets were evident in the Ga reservoir, as expected, and the resultant layer PL exhibited Group II (open tube) behavior with the long wavelength IR contribution weak and strong green emission.

Annealing studies also suggest that recombination centers associated with Ga vacancies are formed. A Group I epitaxial layer whose PL spectrum is shown in Figure 5(a) was annealed in *vacuum* at a temperature of 550° for 18 hours with a relative reduction in the low energy band [Figure 5(b)]. However, an anneal of this material in a *P ambient* again increased the low energy-band intensity [Figure 5(c)] relative to the green emission.

Thus, we find that the best layers from the point of view of PL results are obtained under a low P pressure, and the worst ones are obtained under conditions resulting in high P_2 (or P_4) partial pressures. It is irrelevant whether the solutions are confined, thus trapping P_2 or P_4, or whether we reduce the hydrogen flow rate and thus build up the phosphorus partial pressure. Furthermore, we find that these effects are reversible in that annealing the material in vacuum removes the low energy band and it can be reintroduced by annealing in a phosphorus-rich ambient. There is little doubt, therefore, that excess phosphorus pressure results in the generation of flaws, presumably connected with Ga vacancies, which manifest themselves by a broad emission band centered at ∿ 7200 Å and reduced green emission efficiency. Material having such emission also yields inefficient diodes. The open-flow growth system was used for all of the devices, unless specific information of a different type was required.

The main conclusions from this part of the work are therefore the following: The phosphorus pressure above the LPE solution during growth exerts a controlling influence on the properties of the material, especially as regards the introduction of defects associated with Ga vacancies. Thus, for optimum efficiency, one should control the phosphorus pressure during growth. Whereas the simple experiments carried out so far clearly show the advantage of open flow growth, it must be pointed out that there may be an optimum P pressure either lower or higher than the one we were working with. This conclusion arises because of the possibility of introducing P vacancies when the partial pressure of phosphorus over the melt is low enough.

The sensitivity of the material to the P pressure provides a clue to the poorly understood reason for the variability in efficiency. Thus in repeated trials, using identical schedules and

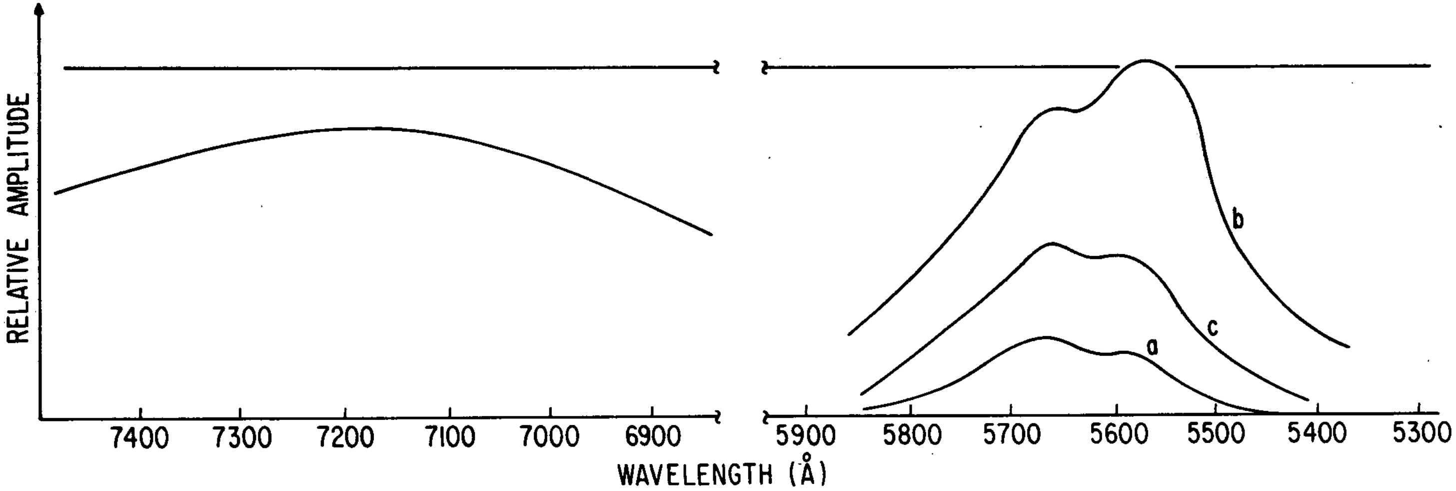


Figure 5. (a) PL of an n-layer grown in a sealed crucible.
(b) The same layer after vacuum anneal.
(c) The same layer after further anneal in phosphorus ambient.

processes, one finds a considerable scatter in the efficiency of the resultant material. Control of P pressure in these runs is only provided indirectly. The present results suggest that the phosphorus pressure should be directly controlled in order to stabilize a heretofore ignored variable.

Several methods were used to nitrogen-dope the material. The most controllable method consisted of placing the solution in the quasi-sealed crucible together with a small quantity of crystalline GaN, and then raising the temperature to 1060 to 1080°C for 5 minutes. After cooling down, the solution is transferred to another boat and used for the open-tube growth of the n-type layer. Another useful technique consists of baking out the solution at 600°C, followed by the addition of nitrogen by flowing NH_3 through the furnace. This avoids the transfer of solutions with the possibility of contamination.

The nitrogen concentration in the GaP was determined by optical absorption using the relationship (Ref. 6)

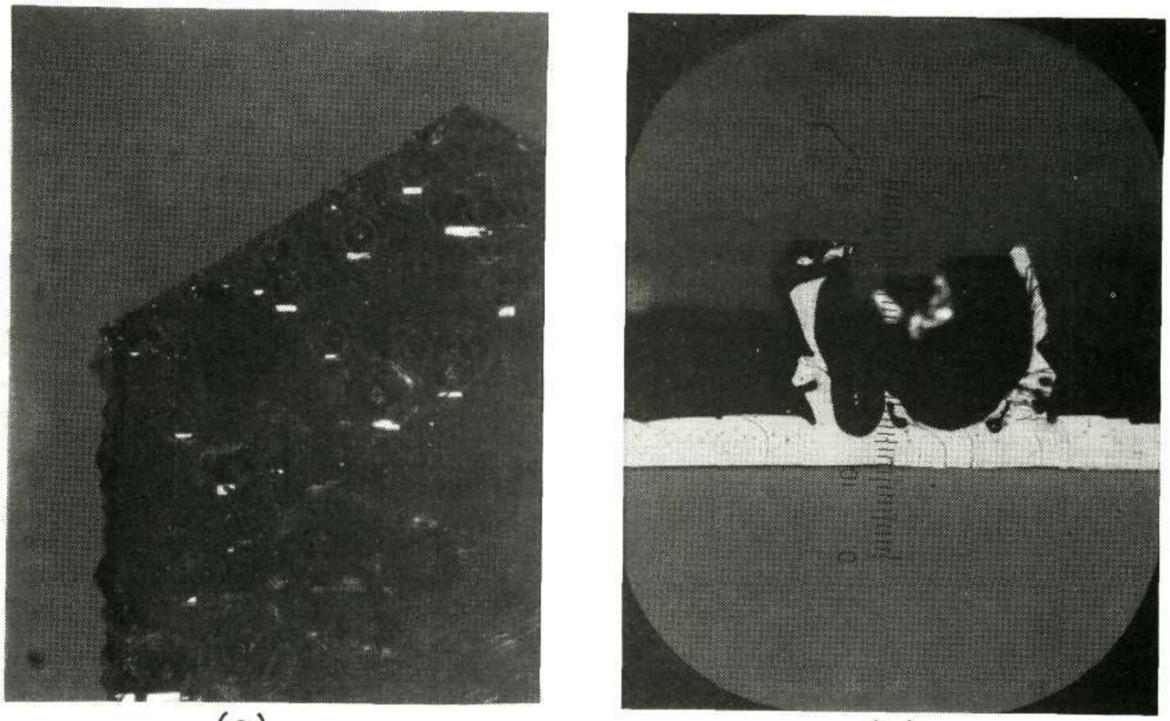
$$N = 1.3 \times 10^5 \alpha_A \frac{\Delta E}{0.2} , \qquad (2)$$

where α_A is the absorption coefficient of the A line at 77°K and ΔE is the full width of the absorption line at the half intensity point (in meV). Typically, the N concentration was 4×10^{18} cm^{-3} in the materials studied as determined by the absorption method. The layer electron concentration is usually in the $2\text{-}6 \times 10^{16}$ cm^{-3} range without intentional donor doping.

It should be noted that the solubility of N is known to be high in GaP (10^{19} cm^{-3}) (Ref. 1), and it would appear that the highest possible doping should be used in order to enhance the green luminescence. In principle, this is possible since the addition of N does not increase the free carrier concentration and does not, therefore, lead to non-radiative Auger recombination. However, excessive concentrations of N lead to disturbances in growth, and the formation of other crystalline forms (Figure 6) indicating the presence of new phases involving N. For the above reason, and also because of the high absorption, an *optimum* N concentration must exist, the exact value depending on the diode configuration.

B. Preparation of p-n Junctions

In order to study the influence of the junction formation method on the diode performance we have prepared three different



(a) (b)

Figure 6. Growth disturbances due to excess nitrogen in the solution. On the photograph, (a) numerous hexagonal "caverns" are seen to grow out of the wafer surface. On photograph (b) a cross section through such a "cavern." (0.001 cm/division.)

types of junctions using similar n-type regions prepared as discussed above. The junctions were formed by zinc diffusion, two-step LPE, and double-bin LPE. The dc efficiencies of the diodes obtained were compared at ∿ 10 A/cm^2 using a standard assembly technique in which a 0.25 mm x 0.25 mm chip was provided with alloyed contacts on portions of the bottom and top surface, mounted on a TO-18 header, and covered with a plastic dome. The green emission was separated from the red emission by the use of a Corning 4-97 filter, while the red emission was separately measured by the use of a 2-58 filter. A calibrated Si solar cell was used in all cases in an integrating sphere. Results are shown in Table I.

1. Zinc Diffused Diodes - Zinc was diffused into LPE layers grown under previously optimized conditions. Various zinc diffusion schedules in sealed ampoules were used with all of them giving similar results. A typical schedule consisted of 1 mg/cm^3 of ZnP_2 at 850°C for 1.5 hours which yielded a junction depth of 7 to 8 µm. Efficiencies for these diodes are typically 0.03% at 10 A/cm^2 to 40 A/cm^2.

Table I

EFFICIENCY OF DIODES SIMILARLY ASSEMBLED

Junction Type	Standard Efficiency* (green only) (%)
Diffused	0.03
Two-step	0.045
Double-bin	0.14

*"Standard" efficiency is the dc value of encapsulated diodes having planar geometry and alloyed contacts, at ∿ 10 A/cm^2.

2. Two-Step LPE - Two-step LPE diodes were obtained by growing a Zn-doped layer onto a previously prepared nitrogen-doped n-layer. The p-layer is grown from a solution containing 5 gm Ga, 0.095 gm GaP, 10 mg Zn, at the tipping temperature of 960° and a cooling rate of 20°/minute. The green diode efficiencies are typically 0.045% at ∿ 10 A/cm^2. For comparison, we note that diodes made using Group I n-layers had green efficiency values of only 0.001 to 0.002%.

3. Single-Step Double-Bin (DB) Epitaxy - The study of diodes made by the double epitaxial process where the junctions are prepared at high temperatures without an intermediate cool down step was motivated by the successful research at RCA Laboratories on (AlGa)As-GaAs heterojunctions (Ref. 7) which utilize this type of double bin growth (Ref. 8) to generate the p-n junctions.

The double-bin growth is carried out in a special quartz and vitreous carbon boat shown in Figure 7. Once the boat is set on the desired cooling schedule, the wafer is moved from bin to bin to produce the layers. The Ga solutions are first prebaked at 1040°C in flowing palladium-diffused hydrogen ($\approx$100 cm^3/min). The solution used for the n-type layer is saturated with nitrogen in a separate heating step before being placed in the bin. The Ga solutions consist of 7 wt% GaP and 0.14 wt% Zn for the p-side and 7 wt% GaP for the n-side with usually no deliberate donor doping. The cooling rate is 7.5°C/min. starting at 1020°C, and the p-n junction is formed at 980°C.

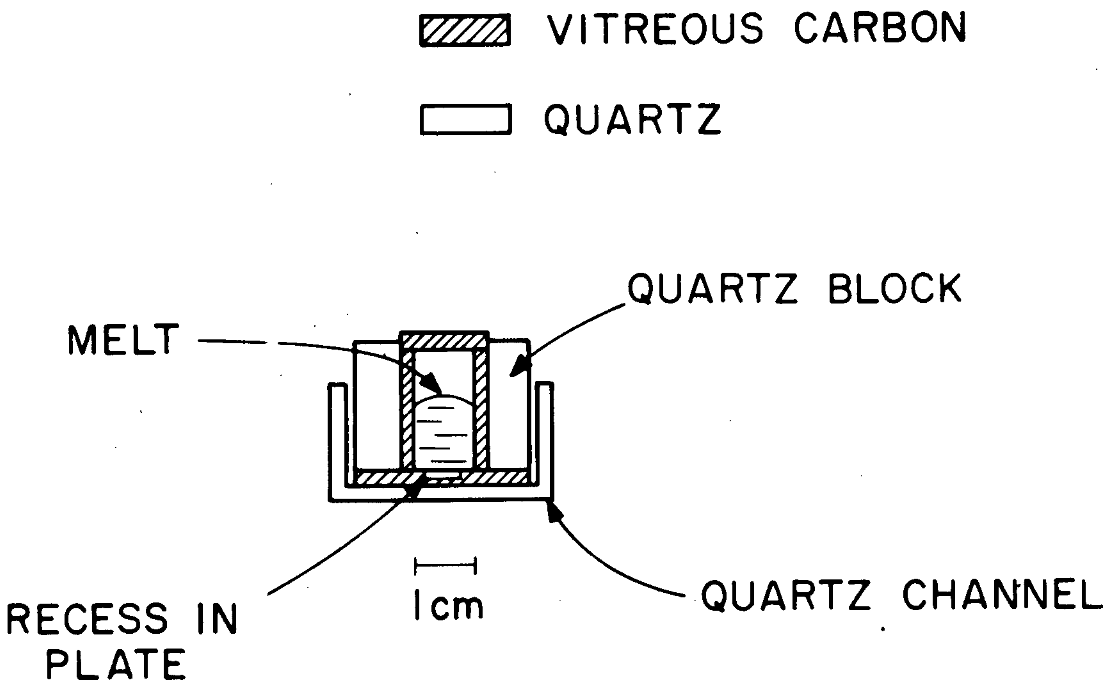


Figure 7. End-view of double-bin boat used in the growth of GaP layers. The slide direction is perpendicular to the page.

The n-type layers, typically 20 μm thick, have a carrier concentration in the low 10^{16} cm^{-3} range as determined from capacitance-voltage measurements. The residual donor impurities are probably sulfur or Si both of which are known to be common contaminants in GaP. The p-region hole concentration is $\sim 5 \times 10^{17}$ cm^{-3}. These double-bin diodes showed the highest "standard" efficiency of all 3 types, about 0.14% at $\sim$ 10 A/cm^2. While diodes made early in this program had a significant red Zn-O component, more recent diodes show overwhelmingly green emission due to better control of residual oxygen contamination.

The reason for the improved green efficiency of the DB diodes compared to other types is believed to be in the better quality of the p-n junction. In part this may be the result of some degree of compensation on the n-side of the junction due to Zn intermixing in the solutions as a result of which the *impurity* concentration on the p and n-sides of the junction are very nearly equal. This means a lower interfacial defect density. Figure 8 shows a typical diode cross section. Since as we mentioned earlier the diffusion length in GaP is so short, the improved crystalline quality will be reflected in a higher overall efficiency. It is of interest to note that in contrast to two step diodes, the DB devices do not improve by post-growth annealing. This suggests that the defect density is already as low as can be expected under this growth condition.

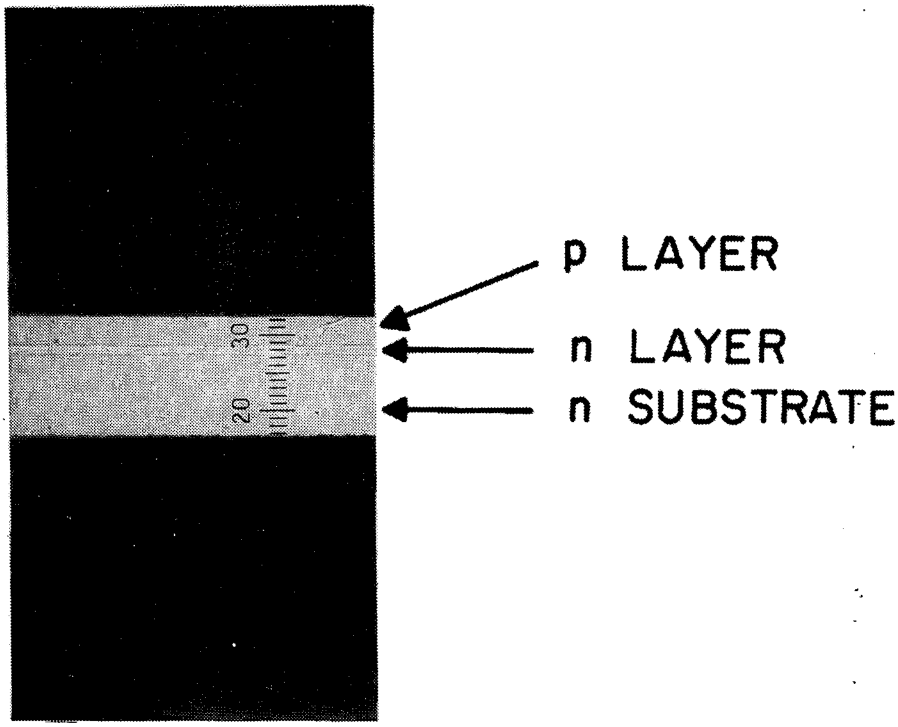


Figure 8. Delineation of a high-efficiency DB junction. (0.001 cm/division.)

With regard to the choice of substrate, we have studied DB diodes grown on LEC substrates as well as on solution-grown platelets with essentially no dislocations. No statistically significant difference in the efficiency could be determined.

Occasionally a DB run was made which produced material with very low EL efficiency. A cleaved and delineated profile from such a wafer is shown in Figure 9. Studies of these layers show that the difficulty arises from the excessive diffusion of zinc from the p-solution into the n-solution. By choosing the sequence of p on n growth, the p-solution is heated to the high temperature required for the n-solution growth, and the zinc vaporizes and may counterdope the weakly doped n-solution. One way of eliminating this problem is to reverse the order and grow the p-layer first. Indeed, several reverse order runs were made showing no contamination, but the efficiency, so far, has been lower than in the p on n case. The best answer thus appears to be a careful control of the heating cycle, a careful control of the zinc content in the p-solution and good boat design to reduce the chance of zinc cross-contamination. It should be noted that diodes were also made by flowing zinc vapor over the solution (instead of adding Zn in metallic form) with results approaching those obtained from good DB runs.

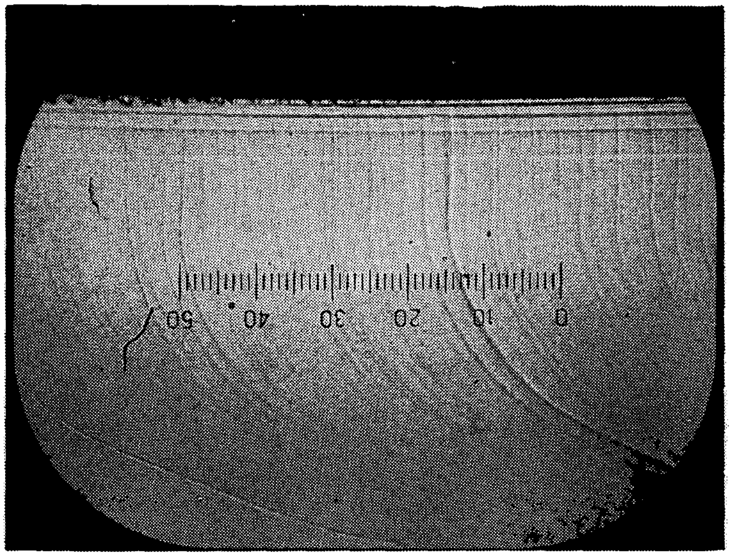


Figure 9. Multiple junctions produced inadvertently in DB growth by uncontrolled Zn diffusion. (0.001 cm/division.)

C. Other Acceptors in GaP: Be and Mg

The problems we have described in connection with Zn in the double-bin work have caused us to examine other acceptors. In general a suitable acceptor should have a high solubility in GaP, should not form precipitates, dissolve readily in Ga, and have a low vapor pressure and a low diffusion rate. In several respects Be meets these requirements but it diffuses too rapidly and its solubility in Ga appears to be low. P layers doped with Be were grown using compositions similar to those used with zinc, and two-step diodes were produced with efficiencies not significantly different from their zinc-doped counterparts. However, the question of the life of such diodes may be a problem as it was found that GaAs:Be diodes degrade rapidly under forward bias operation (Ref. 9).

With regard to the Mg, its vapor pressure is lower than of Zn and the diffusivity is also expected to be lower. Mg doped layers were grown from a solution containing 1.9% by weight of GaP, and 0.13% Mg. A tipping temperature of 960° and slow cooling rates were used. It was found that the solution is altered in appearance, compared to a Ga-GaP solution, because various decomposition products give it a coroded appearance. At the end of a run, one often sees bright green crystallites floating on the Ga surface, which rapidly disappear on exposure to laboratory air. The "standard" diode efficiency obtained in a limited number of runs was ∿ 0.03%.

One interesting property of Mg is that no Mg-O pair emission analogous to the Zn-O pairs is observed at room temperature, and these diodes do not, therefore, have any red emission. The stringent requirements on solution purity concerning oxygen contamination can therefore be relaxed.

D. GaP-(AlGa)P Heterojunctions

The room-temperature lattice constants of GaP and AlP (E_g = 2.45 eV) are close (5.40 Å for GaP vs. 5.462 Å for AlP) and it appears attractive to investigate various simple possibilities to improve the efficiency of the GaP diode emission such as: (a) taking advantage of the GaAlP-GaP heterojunction in order to improve the injection efficiency of holes into n-type material, and (b) providing a window over the GaP homojunction in order to improve the external coupling.

GaAlP layers were grown using various melts and schedules, a typical one consisting of 10 gm Ga, 0.65 gm GaP, 50 mg Al, a tipping temperature of 1080° and a cooling rate of 0.25°/min.

(a) Several attempts were made to utilize this scheme, but the results were not encouraging. In some cases, it is possible to understand the reason for this; for example, as shown in Figure 10, an $Al_xGa_{1-x}P$ p-type layer was grown onto an n-type GaP layer. An etch of a cleaved edge shows a line of what appear to

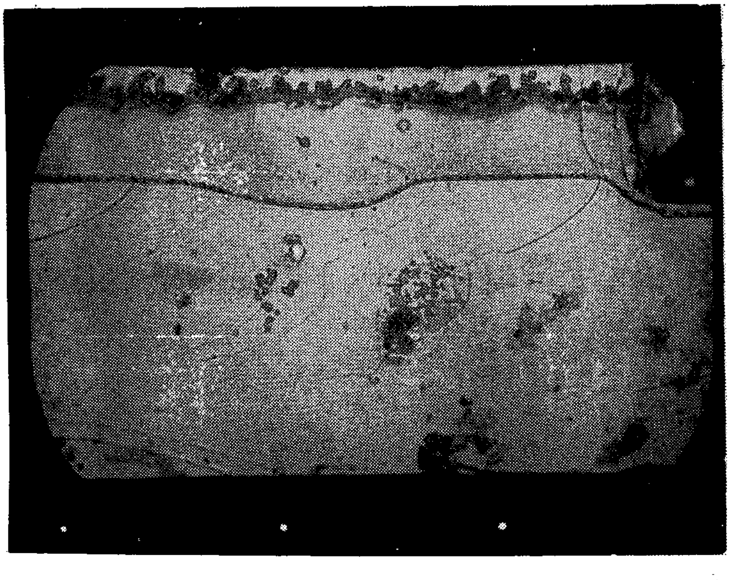


Figure 10. Heterojunction between (AlGa)P and GaP "decorated" with impurity precipitates.

be decorated dislocations, and the junction emits very little light. This suggest the presence of a precipitate due to a chemical reaction associated with aluminum or due to a lattice mismatch at the growth temperature. Indeed, the variation of the lattice constant with temperature of AlP has not yet been measured.

A more successful approach consisted in placing the junction into a graded region; i.e., one where the Al to Ga ratio varies smoothly. Although fairly good light emitters were made, and the possibility of eventually obtaining superior performance could not be ruled out, we have not found the added complexity to be justified in the result.

(b) Attempts made to place a window near the GaP homojunction also failed to yield higher efficiency diodes. Two explanations suggest themselves, one being that the strain due to the heterojunction affects the homojunction, and the other being that refractive index discontinuity prevents the exit of some of the light. The second explanation gains some support from a microscopic examination of an emitting diode containing such a structure.

Figure 11 shows a cross section of a typical heterojunction diode under forward bias. The large dark region is the substrate

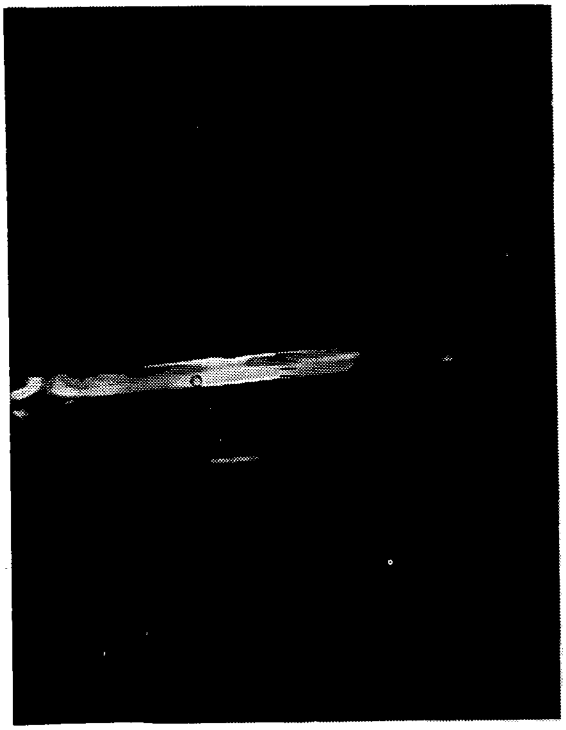


Figure 11. Reflection from an internal heterojunction between GaP and (AlGa)P.

consisting of p-type GaP, the next layer is p-type (AlGa)P, and above the bright region is an n-type (AlGa)P layer. As can be seen there is an extremely sharp dividing line between the substrate and the (AlGa)P which may be due to the reflection at the heterojunction boundary.

In summary, the poor results obtained with the GaP-(AlGa)P heterojunctions may be the result of a greater than expected lattice parameter mismatch at the growth temperature. As the material cools to room temperature, strains can be frozen into the active region of the device and dislocations can be formed to relieve the lattice misfit at high temperatures. As a result, the radiative efficiency of the GaP active region is greatly reduced. Gallium phosphide efficiency is likely to be far more sensitive to the introduction of nonradiative centers than a direct bandgap compound like GaAs because the radiative processes in GaP:N constitute but a small fraction of the overall recombination processes. Undesirable reactions due to the presence of Al may also contribute to reduced efficiencies, and the internal light reflection may in some cases reduce the external efficiency of our otherwise efficient junction.

III. DEVICE FABRICATION

The basic device problem in LEDs is that high external *efficiency* requires that the greatest possible number of photons be incident normal to the emitting surface, whereas high *brightness* requires all the emission to come from a small area. These two requirements conflict. While the efficiency can be greatly increased by shaping the diode into a hemisphere with a small circular junction area at the center, its brightness is low because the emission is spread out over the hemispherical surface. A high brightness emitter is obtained from a planar diode with the junction parallel to the surface*. Under this condition most of the photons incident on the surface within the critical angle will be able to leave the crystal, with the distribution of radiation being approximately Lambertian. Photons outside the acceptance cone undergo multiple reflections and become absorbed due to the various loss mechanisms in the diode. Thus diodes with planar geometry are bright but relatively inefficient, while diodes with dome geometry are efficient but not as bright.

It is generally advantageous to use a planar geometry for practical diodes and within its limitations it is possible to optimize the diode efficiency by the proper choice of metallization. Obviously if the contact blocks the light the device output will suffer, but contact design depends on the resistivity of the material because a high resistivity leads to current crowding under the contact. Thus, an optimum geometry depends on the materials parameters.

A. Diode Design for High External Efficiency

In Section II, we compared the efficiency of diodes fabricated in a standard way in which a significant fraction of the internally generated radiation is reabsorbed. While such a comparison is useful in determining the best process for diode fabrication, it is of equal importance to determine as closely as possible the internal efficiency by studying diodes where the coupling between the internally generated radiation and the outside is optimized without consideration of surface brightness.**

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*We ignore edge emission which, although the brightest, is only justified in special cases.

**The highest previously reported GaP diode efficiency of 0.6% at 80 A/cm^2 for single epitaxial material on a solution-grown platelet (Ref. 1) was obtained with a diode where emission was obtained from both the top and bottom of the diode, by bonding a chip to a glass plate, or by suspending it by contacting wires into free space.

The diode construction used to obtain the highest possible efficiency from a diode is shown in Figure 12. The basic feature is a small p-side contact, a mesa construction, and a small n-side contact with the diode mounted on a reflecting white ceramic base. The whole diode is encapusulated in epoxy. Such diodes can be operated dc to a current density of about 30 A/cm^2 but must be pulsed above that value to eliminate efficiency loss due to the junction heating. In the diodes which were measured pulsed the green emission increased superlinearly with current up to at least 200 A/cm^2. The green emission L varied with junction current density J as follows

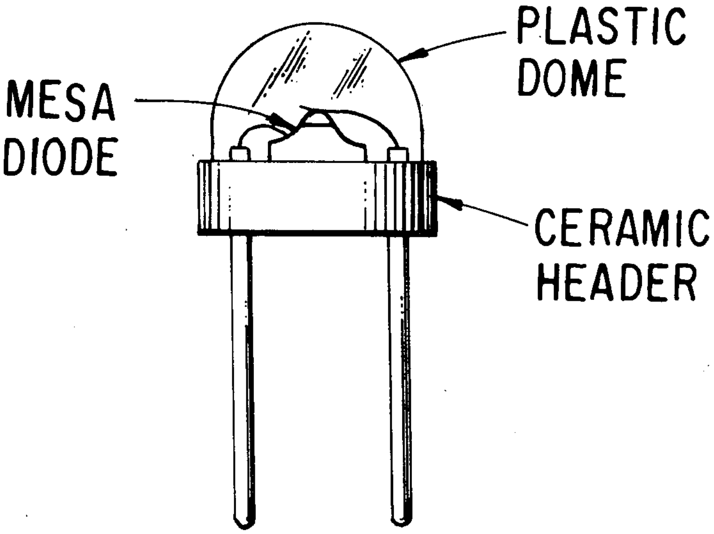

Figure 12. Mesa diode construction.

$$L = \kappa J^n \tag{3}$$

with n between 1.47 and 1.49, and K a constant. This superlinear dependence is indicative of the presence of non-radiative recombination processes which do not increase as rapidly with current as the radiative ones involving the nitrogen centers.

The diode efficiency η at a given current density is given by

$$\eta = C \frac{L}{AJ} = \frac{CK}{A} J^{(n-1)}, \tag{4}$$

where C is a constant and A is the junction areas. Thus, the diode efficiency increases with increasing current density in the range where the light output variation with current is superlinear.

Figure 13 shows the light output as a function of the diode current of a DB diode optimized for emission efficiency with a better than 12:1 green to red emission ratio.at > 30 A/cm^2. The value of n in this diode is 1.49. The absolute efficiency as a function of diode current density for the same diode is plotted in Figure 14. The dc value is seen to saturate near 0.22%, whereas the pulsed value continues to climb to 0.7% at ∿ 200A/cm^2 which is the highest value obtained in the program and a factor of 2 higher than reported for double epitaxial diodes at the same current density (Ref. 1).

B. Numeric Displays

It appears likely that LED displays will be unsurpassed in respect to brightness, cost, and ruggedness, as long as they are designed for close viewing by individuals. For such individual displays, a numeral size of 3 to 4 mm is perfectly adequate, as it allows easy reading at normal viewing distances. Both monolithic and seven segment displays were made in the course of this program and these will be described here.

1. Monolithic-Diffused Display - The diffusion is carried out through a mask produced by deposition of SiO_2 and Si_3N_4 layers using photoresist techniques. Diffusion confined by the mask is illustrated in Figure 15. Details of one segment of the display are shown in Figure 16. The dimension of the display is 4 x 2.3 mm (Figure 17). The current requirement is greater for these diffused displays than for the discrete seven-segment display using epitaxially grown junctions - being ≈ 50 mA per segment compared to 20 mA (see Section III. B. 2. below).

2. Segmented Display - The design adopted uses plane geometry with reduced-area top contacts and partially reflecting contacts on the bottom. This is illustrated in Figure 18 which shows the design of a typical 0.3 mm x 1.1 mm bar used in the seven-segment display. The bottom contact is an "ohmic" ring around the periphery with a reflector through the center, and the top contact is an ohmic center bar. The current flow and the maximum light generation is also shown in Figure 18. The arrangement of the contacts is such that the current is forced outward from the center bar forming the top contact. In this manner, the brightest region is only slightly blocked by the contact, and light striking the bottom is reflected upward for a return trip. The patterns used are applied using standard photolithographic procedures. This involves SiO_2 deposition, photoresist coating, delineation, metallization, and stripping of unwanted metal.

In the fabrication of displays, it is important to design the device for high contrast between the on and off state. This generally requires a dark background. We have solved the contrast

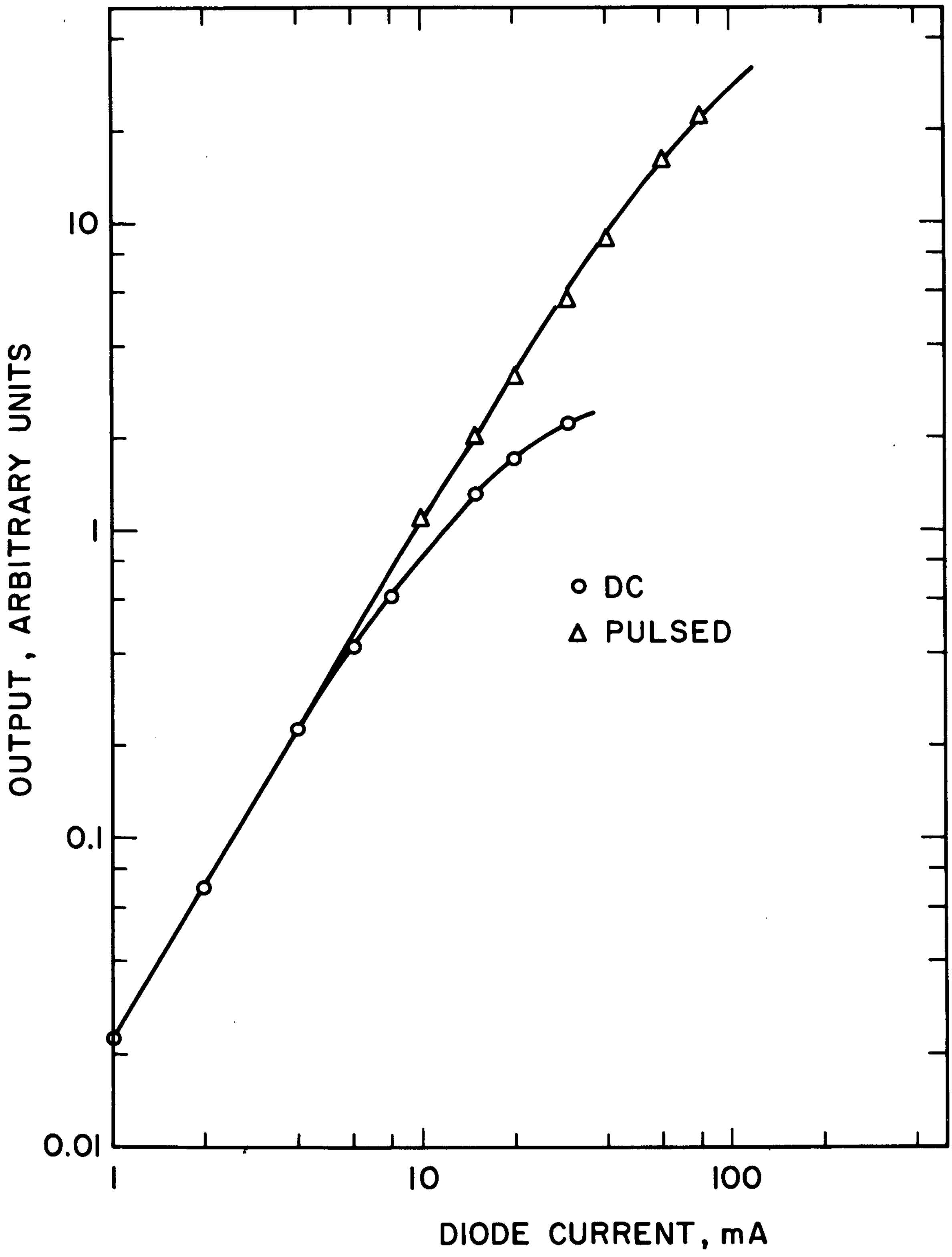

Figure 13. Relative output from a high efficiency DB diode as a function of diode current.

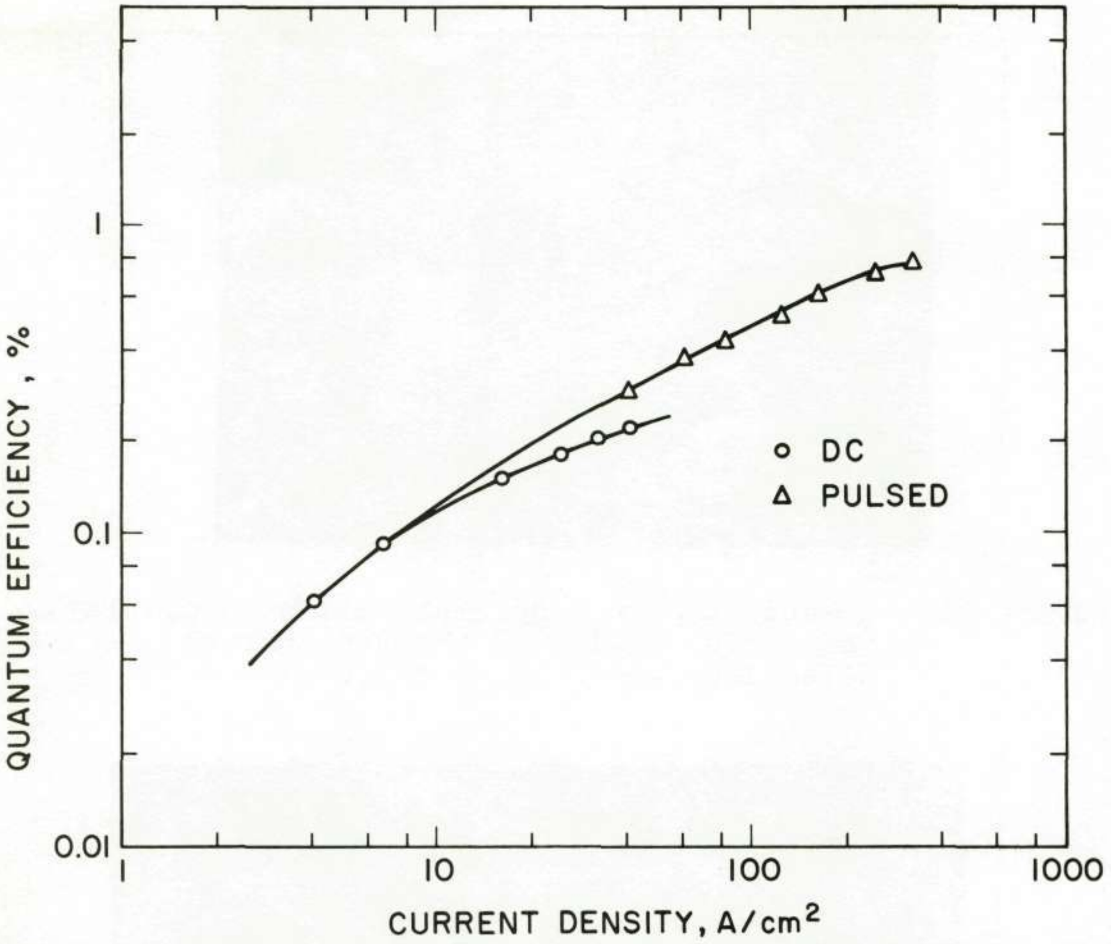

Figure 14. Quantum efficiency as a function of current density of a high-efficiency DB diode with minimal internal loss. The green/red emitted power ratio is greater than 12:1 for current densities of $\geq$ 30 A/cm^2.

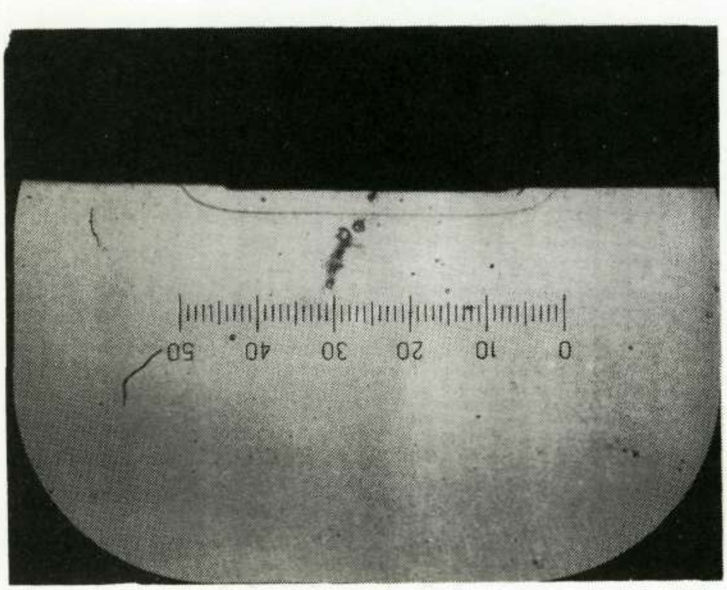

Figure 15.

Junction diffused through openings in a SiO_2, Si_3N_4 mask.

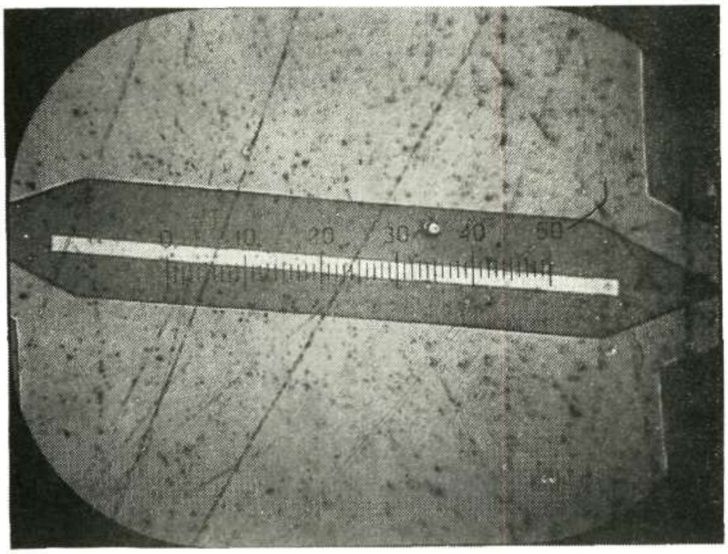

Figure 16. A segment of a monolithic-diffused display. The center stripe is the top contact. Dimensions are 0.28 mm x 1.6 mm.

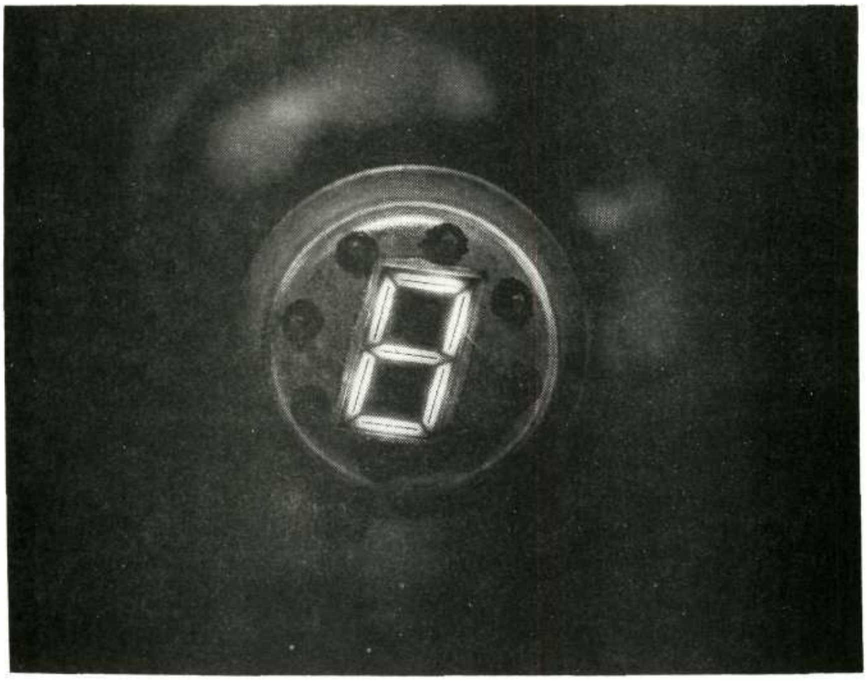

Figure 17. Monolithic-diffused display (4 x 2.3 mm).

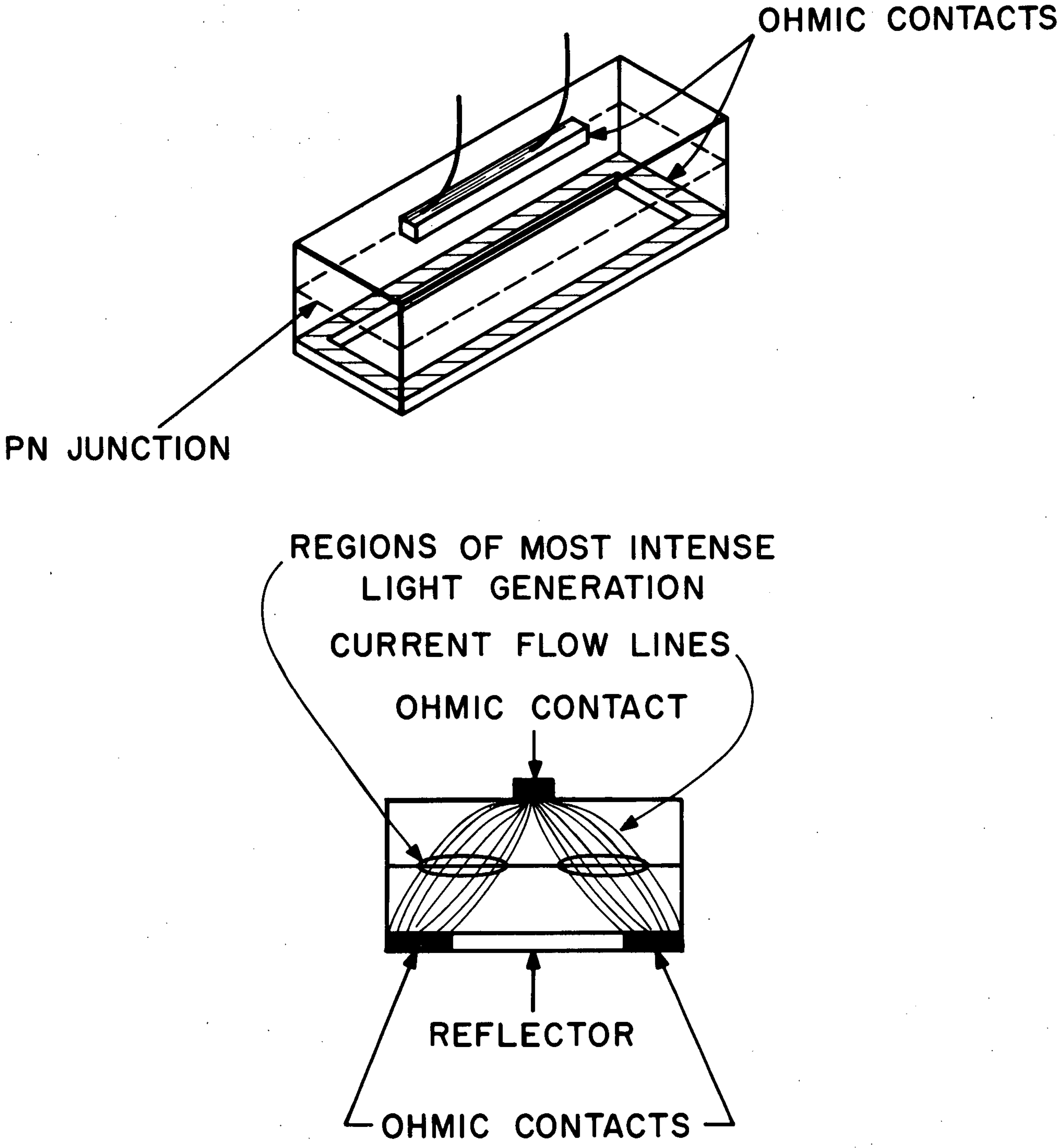

Figure 18. Structure of segmented display showing contact arrangements and current flow.

problem by mounting the bars on nickel-plated headers. The nickel is deposited from an electroless plating bath, and if the header is given a dilute nitric acid etch, the surface assumes a black color. Bars mounted on such a surface show excellent contrast (Figure 19). Brightness at 20 mA per segment was calculated to be 400 fL. The segmented display has the advantage over the monolithic one in that higher efficiency material can be prepared epitaxially than by diffusion thus reducing the required current. Furthermore, no material need be wasted between the segments. Balancing these advantages are the lower batch fabrication costs of the monolithic display which is a real advantage if very small numerics are needed.

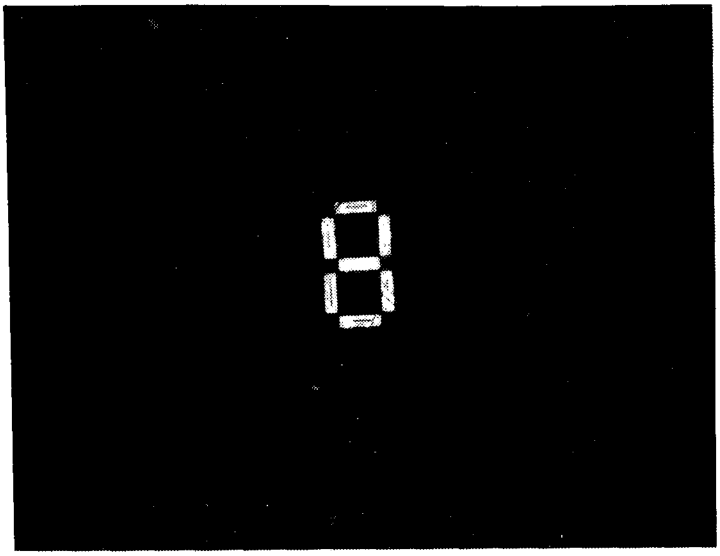

Figure 19. Segmented display.

3. Photolithographic Techniques Applied to Individual Emitters

While the small mesa construction described earlier is useful for determining the ultimate diode efficiency, practical emitters require larger areas with distributed contacts to minimize the losses at the contacts. Thus considerations similar to those mentioned in the discussion of segmented displays have been applied to single diodes. Several contact configurations, i.e., comb, (Figure 20) cross, and ring structures were tried, the most efficient being the ring structure (Figures 21 and 22). The bottom contact for single diodes is most conveniently made by a partially reflecting base either as described for the segmented bars or by an array of ohmic dots in a reflecting surround. Such structures provide the best compromise between efficiency, brightness, and cost.

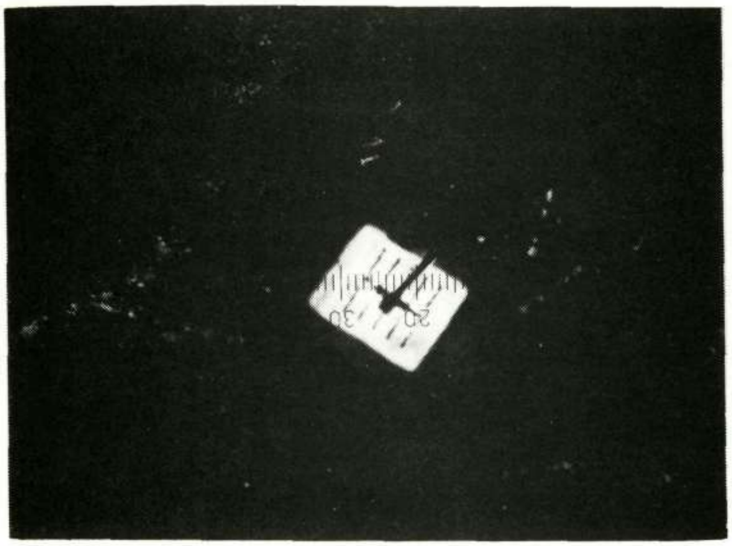

Figure 20. Comb-type ohmic contact.

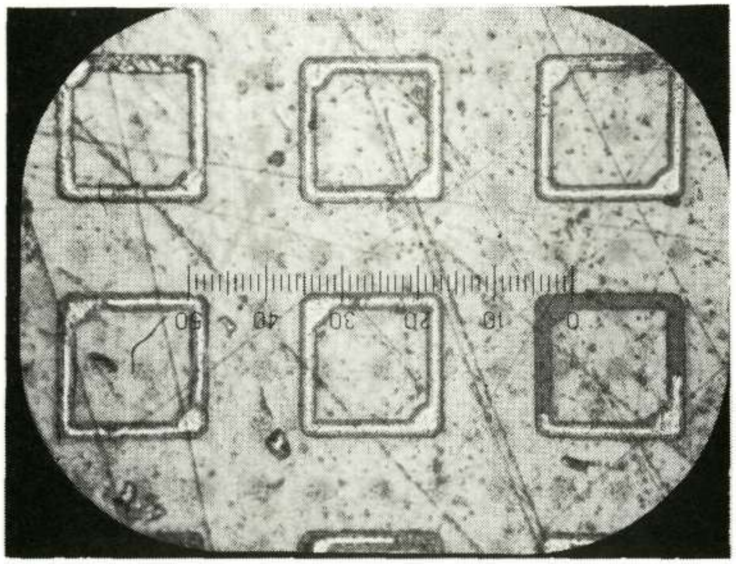

Figure 21. Ring contacts after sintering into the wafer.

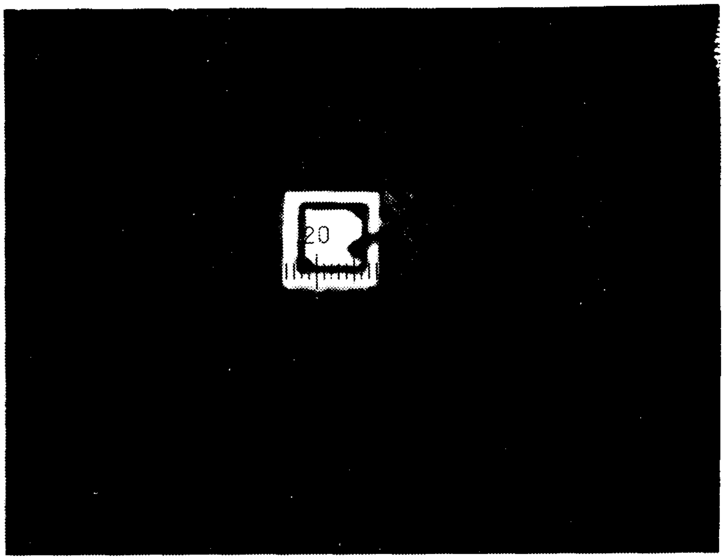

Figure 22. Ring contact diode.

IV. CONCLUSIONS

The overall objective of this program was to demonstrate a green-emitting GaP diode efficiency of 0.5% or higher at room temperature. This has been achieved using an improved process for the fabrication of these diodes. Under pulsed excitation (to minimize junction heating) an efficiency value of 0.7% has been achieved at 200 A/cm^2. The above value is achievable using both LEC and SG substrates, no significant difference having been found between diodes grown on the two substrates. At lower current densities (33 A/cm^2) a value of 0.2% has been achieved under dc operation. These are the highest values reported to date under their respective modes of operation for double-epitaxial diodes. The highest previously reported value (Ref. 1) was 0.6% at 80 A/cm^2 in a single epitaxial diode on a solution grown platelet, and 0.34% at 200A/cm^2 for a double epitaxial diode.

A study of the techniques for preparing n-type material and junctions which yield the most consistent high diode-efficiency values has highlighted the role that Ga vacancies and/or associated defects play in reducing the green luminescent efficiency of n-type GaP. A useful method of obtaining good quality material has been developed. We have shown that junction formation at high temperatures in a process where the n to p transition occurs without removing the substrate from the furnace yields devices superior to those obtained by diffusion or double epitaxy in the conventional manner previously used for GaP junction formation. While the reason for the improvement is not definitively established, it is believed that reduced non-radiative recombination occurs in such "double-bin" grown diodes, possibly because of a better lattice constant match at the p-n junction. It is very significant that **similar efficiencies** have been obtained on diodes grown using large-area melt-grown GaP and on dislocation-free platelets grown from Ga solution.

The efficiencies of structures containing (AlGa)P-GaP heterojunctions were investigated. The results were disapointing in that the efficiency was lower than in homojunctions. The partial explanation may be that the lattice parameter mismatch at high temperatures is significantly worse than at room temperature with the resultant formation of a high density of non-radiative recombination centers.

Both Mg and Be have been investigated as possible substitutes for Zn. There appears to be no obvious advantage to their general use at this time, although Mg may have some special applications.

Various structures have been studied for numeric displays. A monolithic green GaP numeric element has been made for the first time by Zn diffusion. Segmented displays have also been made with an estimated brightness of 400 fL at a drive current of 20 mA per segment having a length of 1.1 mm and width of 0.3 mm.

V. NEW TECHNOLOGY

It was concluded that five reportable items of New Technology had resulted from the contract effort during the period covered by this final report. These are as follows: A. Planar EL Diodes; B. Mg Doped GaP Diode; C. Dark Background for EL Displays; D. Internal Light Reflection of GaAlP-GaP Heterojunction; and E. Quick Removal of Ga from GaP.

A. Planar EL Diodes

Brief Description: A diode structure which lends itself to diffusion technology and yields more efficient light emission.

Detailed Description: Ordinary LEDs have geometries as shown in Figure 23(a). The brightest region is obscured by the contact. A better design is shown in Figure 23(b). It can be seen that the

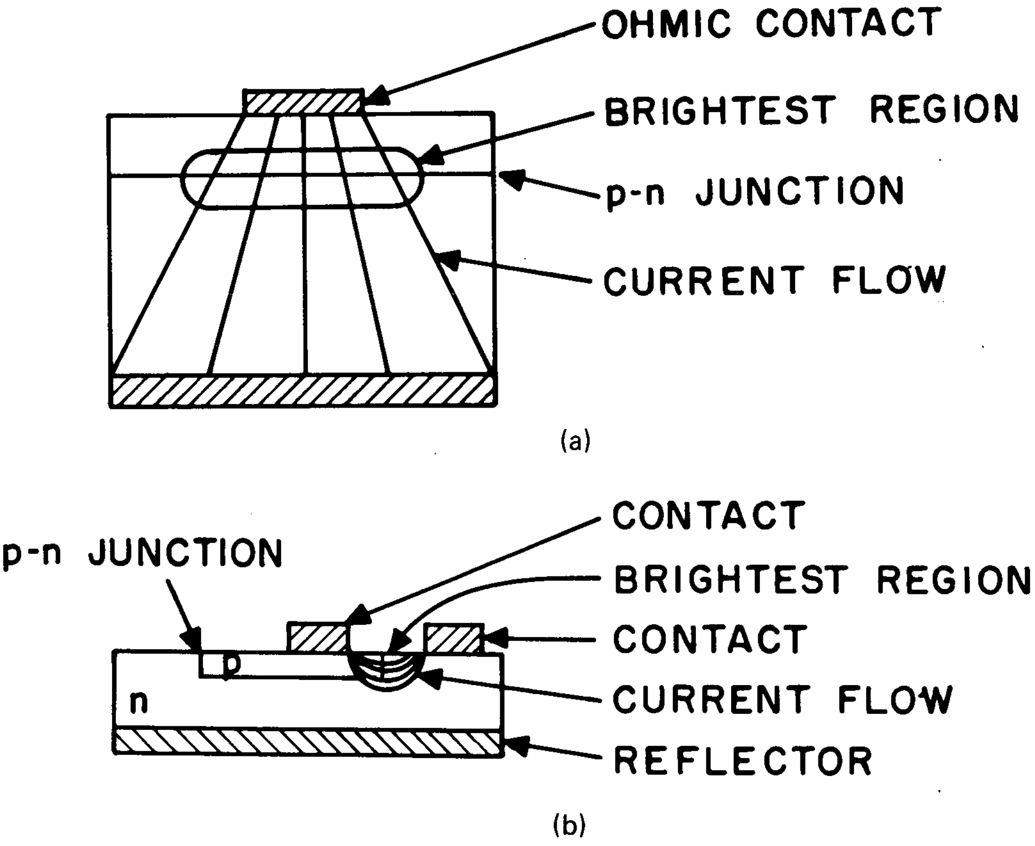

Figure 23. (a) Standard LED geometry showing contact blocking effect.
(b) Planar geometry with no contact blocking.

current is crowded into flowing parallel to the surface. Thus, the region of greatest brightness has been brought away from the contact where it is not blocked. The whole device can be fabricated using planar monolithic technology and all contacts are applied on the same surface. The design is especially effective for matrix arrays.

Applications: This constitutes a promising design both for individual diodes and for diode arrays and may therefore find extensive commercial applications.

Degree of Development: So far this has not been tested, but work is proceeding at present with the aim of demonstrating the capabilities of this design.

Previous Publications: None.

Innovators' Names, Home Addresses, and Social Security Numbers:

Ivan Ladany
18 Robin Drive
Skillman, N. J.
[redacted]

Marvin Dale Moyer
809 Elm Street
Hatfield, Penna.
[redacted]

B. Mg-Doped GaP Diode

Brief Description: Various advantages result from the use of Mg instead of or in addition to zinc in green emitting GaP diodes.

Detailed Description: The customary method of making green emitting GaP diodes is to use Zn as the p-dopant.

1. Since Mg has lower diffusion coefficient than zinc, more abrupt junctions are possible. This is especially useful in building up complex structures consisting of several layers.

2. Either through the gettering properties of Mg (which prevents oxygen incorporation), or because of the absence of Mg-O pairing (as in Zn-O), there is negligible red emission at room temperature. Thus the spectrum tends to be purer than for Zn-doped diodes where there is always some 6900 Å emission due to residual oxygen pairing with zinc.

3. Mg can be combined with zinc in such a way that the junction is formed by diffusion of zinc into n-material, and the doping of the rest of the p-layer is set by the Mg. Thus, very low zinc doping levels can be used - levels so low

ε

that the region would be converted to n-type during the run, which is a common problem with low Zn doping in LPE. At the same time, the Zn level can be kept very low near the junction, which is desirable for high efficiency.

Applications: Various commercial applications arise from the properties described on the preceding page.

Degree of Development: Although several layers suitable for diode fabrication have been grown, the full potential has not yet been explored. The double-doping concept has not been tried in practice. The better spectral purity has been demonstrated. The efficiency is so far inferior to what has been obtained with zinc.

Previous Publications: Quarterly Report.

Innovator's Name, Home Address, and Social Security Number:

Ivan Ladany
18 Robin Drive
Skillman, N. J.
[redacted]

C. Dark Background for EL Displays

Brief Description: Contrast enhancement is accomplished by means of chemical treatment of metallized surface after diodes are mounted.

Detailed Description: Diodes or EL segments are bonded onto a header previously coated with an electroless nickel plate. After mounting, the header is dipped into a dilute HNo_3 solution until the nickel turns black. The etch is short enough and sufficiently diluted so it does not affect the diodes.

Applications: The numeric indicator furnished under the contract has been prepared in the above way. Commercial applications are feasible.

Degree of Development: The feasibility has been demonstrated.

Previous Publications: None.

Innovator's Name, Home Address, and Social Security Number:

Ivan Ladany
18 Robin Drive
Skillman, N. J.
[redacted]

D. Internal Light Reflection at GaP-GaAlP Heterojunction

Brief Description: A built-in heterojunction is used to produce diodes with higher brightness.

Detailed Description: A GaP-(AlGa)P heterojunction represents a jump in the refractive index. If such a junction is incorporated into a diode as shown in Figure 24, the light is reflected upward from the heterojunction toward the surface. Optically, the diode is therefore very thin, and there is less internal absorption with a consequent gain in efficiency. An added advantage is that it becomes simpler to design the bottom contact as it is no longer required to make it optically nonabsorbing.

Applications: This innovation may be incorporated into green GaP diodes for higher efficiency and brightness, although the overall effect on the internal efficiency may be detrimental.

Degree of Development: The feasibility of this idea has been demonstrated, but there has not been a conclusive test on diodes.

Previous Publications: Final Report.

Innovator's Name, Home Address, and Social Security Number:

Ivan Ladany
18 Robin Drive
Skillman, N. J.
[redacted]

E. Quick Removal of Ga from GaP Surfaces

Brief Description: Gallium is readily removed from GaP surfaces through etching in HF:H_2O_2 solution.

Detailed Description: The gallium covered wafer is placed in a Teflon beaker, covered with 10 cm^3 of HF, and H_2O_2 is added slowly until a reaction begins. The beaker is then placed in a hooded sink to both avoid breathing of fumes and to keep the beaker cool as the reaction is violent and exothermic. Gallium is removed in a few seconds. Occasionally it is hard to get the reaction started, possibly because of a passivating layer on the Ga surface. It is therefore helpful to warm the wafer on the hot plate and to repeat the process.

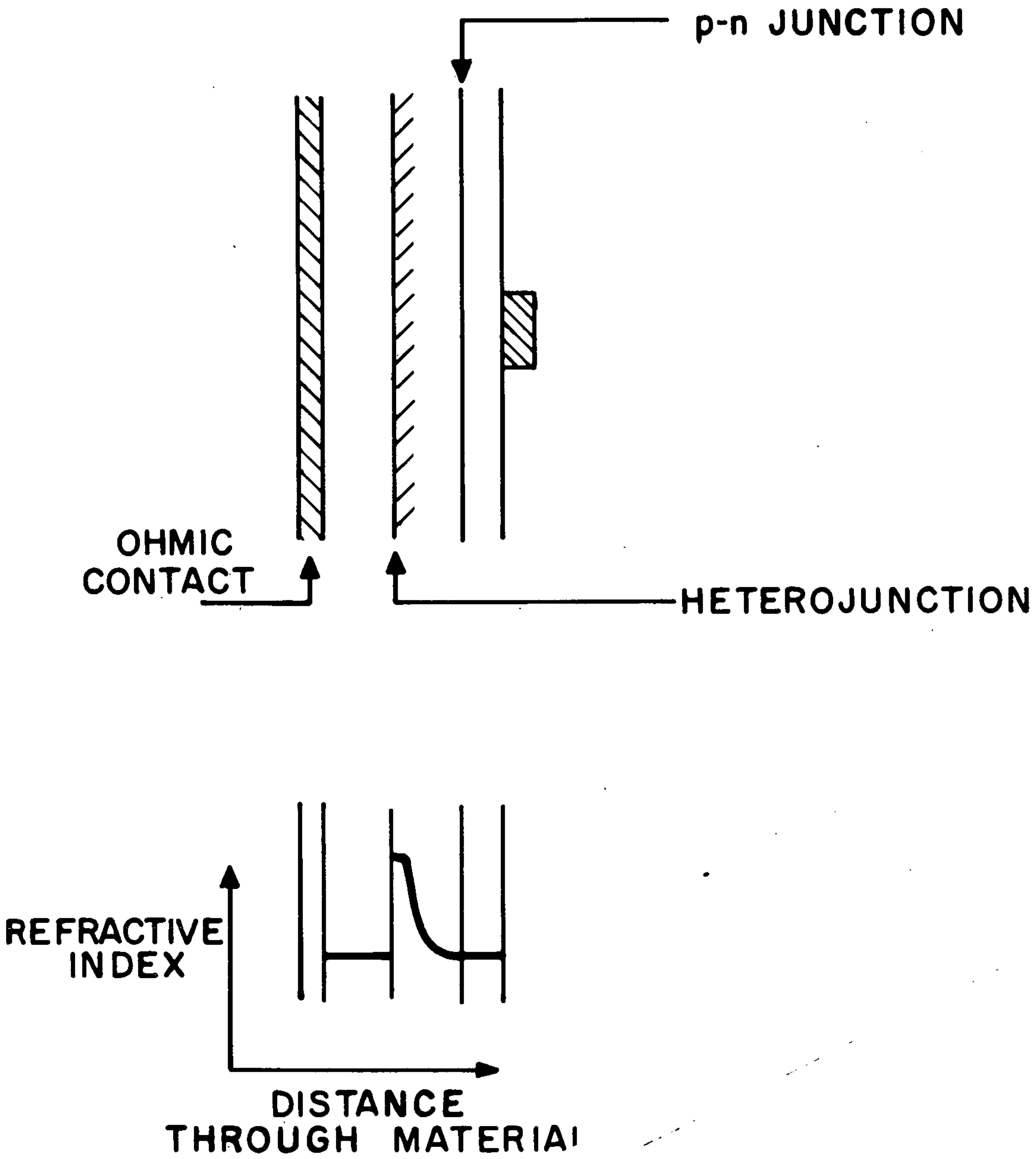

Figure 24. Retractive index jump due to a heterojunction built into a GaP diode.

Applications: Useful as a general laboratory technique.

Degree of Development: It is a quick and convenient way of removing Ga, and is useful whenever the HF:H_2O_2 solution does not attack the substrate to any significant extent. The fumes emitted may be poisonous.

Previous Publications: None.

Innovator's Name, Home Address, and Social Security number:

Ivan Ladany
18 Robin Drive
Skillman, N. J.
[redacted]

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