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Formation of Built-in Light-emitting Junctions in Solution-grown GaP Containing Shallow Donors and Acceptors*

Abstract: The growth of GaP from a gallium-rich solution is described and the morphology and dendritic growth habit of the crystals are discussed. By control of growth conditions it was possible to produce built-in junctions in crystals doped with the shallow donors, S, Se, or Te, and the shallow acceptor, Zn. Green junction electroluminescence of higher efficiency than has been reported heretofore was observed from these structures. The effective segregation coefficients for the above impurities in GaP were determined by radiochemical techniques. On the basis of differences existing between these coefficients for the donor and acceptor dopants, and with the assumption of a two-step growth process, a mechanism for the formation of the junctions during precipitation of the crystals from solution is set forth.*

* The electrical and luminescent properties of these junctions are described by M. H. Pilkuhn and L. M. Foster in a companion paper (page 122 of this issue).

Introduction

Junction electroluminescence from gallium phosphide diodes has been observed by many workers.[1–6] The forbidden bandgap of GaP is 2.24 eV at 300°K[7] and thus can accommodate radiative transitions in the visible range from red through green. Because of this favorable bandgap, several early investigations of GaP luminescence were concerned with development of usable, visible light sources. Success was precluded, however, by the very low quantum yields of light from the devices. Although a few unsubstantiated high values for the efficiency are found in the early literature, the real situation prior to 1964 was probably best described by Gershenzon et al.,[8] who reported total external yields of 10^{-6} to 10^{-5} at room temperature from diodes prepared in various ways.

Gallium phosphide melts at 1465°C under its phosphorus dissociation pressure of 35 atmospheres[9] and development of a technology based on this compound has been hindered by difficulties in growing suitably doped single crystals by the conventional Bridgman or Czochralski techniques. Graphite was the container material most commonly used in work reported in the early literature, and contamination with carbon was always suspected. Polycrystalline GaP ingots can be grown from off-stoichiometric Ga-GaP melts at somewhat reduced temperature and phosphorus pressure, but care must be exercised to prevent the inclusion of free gallium. Frosch and Derik[10] reported partial success in regrowing such polycrystalline ingots by float zoning under phosphorus pressure to obtain large monocrystalline areas.

Very early, Wolff et al.[11] employed the method of regrowth of previously synthesized GaP from dilute Ga-GaP solutions and demonstrated electroluminescence in it for the first time. In 1964, Grimmeiss and Scholz[12] employed the same method to prepare small irregular platelets doped with zinc and oxygen. Diodes made from this material showed red (1.77 eV) electroluminescence with higher efficiencies than had been observed previously in that band, and renewed interest was generated in GaP as a practical electroluminescent material. In particular, we recognized the desirability of now obtaining efficient luminescence in the green, where the eye is most sensitive.†

Almost all recent workers used the Wolff method to obtain GaP crystals. The reason is largely practical, in that this method gives a simple, partial answer to the growth problem for this difficult material. Certain other

† An external efficiency of 10^{-2} in the red (1.77 eV) is visually equivalent to one of about 10^{-4} in the green (2.21 eV).[13]

features of the method should be pointed out, however, for they might be important for the production of luminescent diodes. For example, the relatively low temperature of growth greatly lessens the possibility of contamination of the crystals by the container material, and the large excess of gallium solvent dilutes or extracts many of the impurities brought in with the original GaP charge.

Of possibly greater significance is the unusual growth habit of the platelets grown from solution and the nonuniform distribution of dopants during growth. Evidence of such segregation was reported by Wolff et al.,[11] and later by Grimmeiss and Scholz,[12] who observed that light was occasionally emitted from internal structures or boundaries in their diodes, as well as from the intentionally formed alloy junctions. Thomas et al.[14] observed that different regions of single crystal plates of solution-grown GaP were of different electrical type as a result of segregation of unidentified impurities.

We have found that "built-in" *p-n* junctions can be deliberately formed in solution-grown GaP platelets by controlling the growth conditions in such a way as to enhance segregation of electrically active impurities. When S, Se or Te is added as the donor impurity and Zn as the acceptor, green electroluminescence (2.21 eV) can be produced under forward bias with higher efficiency than has been reported in this band heretofore. This paper concerns the mechanism of formation of such junctions.

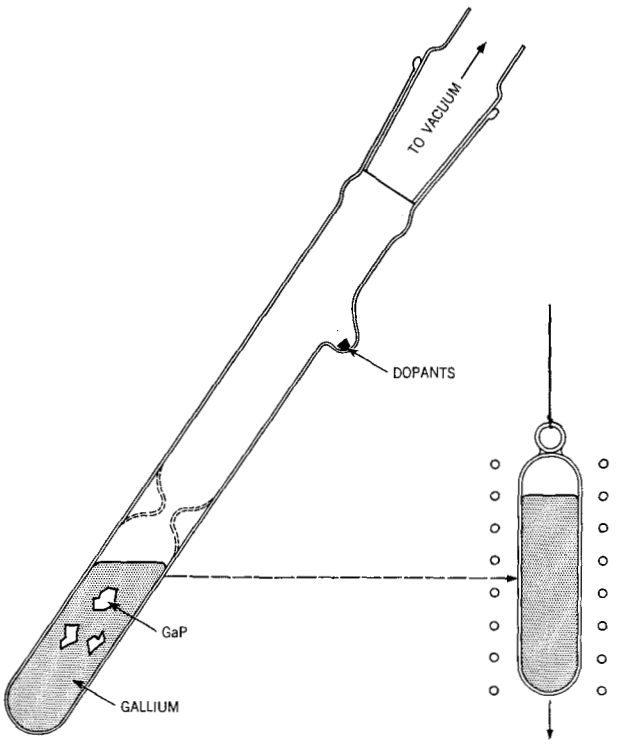


Figure 1 Apparatus for growing GaP platelets from gallium solution.

Experimental

• *Crystal growth*

A Ga-GaP composition was chosen to give an adequate yield of crystals at a temperature not yet high enough to cause excessive attack on the quartz container. A convenient temperature range was 1100–1125°C, where the GaP solubility is 10–12 percent (weight).

The exclusion of oxygen from the system was accomplished by flaming the quartz container tube shown in Fig. 1 under vacuum prior to addition of the dopants. The latter were contained in the depression near the top of the tube during the outgassing so they would not be lost by volatilization, and later were added to the melt by rotating the tube about the greased joint. The tube was then sealed at the constriction shown.

The polycrystalline gallium phosphide for the charge was either purchased (from the Monsanto Chemical Company) or synthesized from the elements in a graphite boat and grown by the horizontal Bridgman technique. In a typical experiment, one gram of GaP and 10 grams of gallium were employed. Zinc was added as the acceptor dopant. Sulfur, selenium, and tellurium were *n*-type dopants used in the study of green emission; these were added either as the elements or as the respective zinc or gallium compounds. Gallium oxide was added when the effect of the deep donor oxygen level on the efficiency of green-emitting diodes was to be studied (see the companion paper, page 122). Since only very small amounts of *n*-type dopants were required, these were usually added as the respective zinc compounds evaporated onto quartz slides. In some experiments, however, *n*-type doping was accomplished by adding an aliquot of heavily doped crystals as part of the charge.

The sealed capsule was supported in a vertical-tube furnace at a temperature about 10–20 degrees above the saturation solubility temperature for the particular mixture and was held at that temperature for about two hours to ensure complete solution of the GaP. It was then lowered out of the furnace with a lowering time of 40 minutes being typical. The GaP crystals were recovered from the excess gallium by boiling them in 1:3 HCl — H_2O.

• *Distribution of dopants*

A series of crystal growth experiments was carried out using radioactive zinc, selenium, and tellurium in order to determine the distribution of these elements between the gallium and GaP. The growth conditions were identical to

Table 1 Distribution of dopants between Ga and GaP.

Exp't. No.	Dopant	Total Ga (grams)	Total GaP (grams)	Total Dopant (grams)	Dopant in GaP: Total (grams)	Dopant in GaP: Atoms per cm³	k_{eff}[a]
1	Zn-65	10.017	1.002	0.0165	0.000076	2.86×10^{18}	0.046
2	Zn-65	10.024	0.996	0.0167	0.00012	4.40×10^{18}	0.072
4	Zn-65	10.010	1.000	0.0164	0.00013	5.00×10^{18}	0.079
2	Se-75	10.023	0.996	0.000208	0.00012	3.69×10^{18}	5.8
3	Se-75	10.026	1.001	0.000203	0.00014	4.26×10^{18}	6.8
4	Te-125	10.010	1.000	0.00179	0.00046	2.20×10^{18}	2.6

[a] Ratio of dopant in 1 gram of GaP to that in 1 gram of Ga, determined on separated components at room temperature.

those in experiments where the same non-radioactive elements were used as dopants. A quantity of the recovered crystals were carefully handpicked to avoid inclusion of any gallium selenides or tellurides in the samples. They were then ground and acid-leached several times until the specific activity remained constant within a few per cent, indicating that all of the free gallium, and all of the dopants dissolved in it, had been removed.

Table 1 shows the results of these experiments. It includes the individual weights of the various components for the reason that the effective distribution coefficients (k_{eff}) are expected to apply only in experiments where those weights are duplicated, along with the ampoule geometry, cooling schedule, etc. Since the dopants segregate in the crystals in a non-uniform manner, this measurement of their gross distribution between the liquid and solid gives only average values for the distribution coefficients, k. These average values are useful, nevertheless, for they give information as to the expected carrier concentrations and the degree of compensation within the crystals and should apply in a qualitative way to GaP crystal growth by other techniques.

Although no similar experiment was performed to determine the distribution of radioactive sulfur, the trend indicated by tellurium and selenium would be expected to continue and k_{eff} for sulfur should be very large.

- *Diode fabrication*

The crystal plates exhibited very diverse morphologies. Since it was not possible to produce uniformly a single type of individual, it was necessary instead to cleave sections out of larger crystals at locations where experience had shown that diodes with fairly reproducible properties could be obtained. Diodes were made by applying ohmic contacts to these pieces, using Au–5% Sn and Au–1% Zn on the n- and p-regions, respectively. The contacts were applied on a strip heater in a forming gas (90% N_2–10% H_2) atmosphere. In order to determine the correct positioning of the contacts, part of the crystal would be contacted on the two surfaces with p and n alloy dots, respectively. An adjacent part of the crystal would then be contacted with the dots in the opposite order, and the best arrangement would be selected on the basis of the electrical and luminescent characteristics of the diode.

Results and Discussion

- *Crystal morphology*

Gallium phosphide crystals grown from dilute gallium solutions have the typically dendritic morphology that is characteristic of precipitates from almost all dilute solutions or alloys where the cooling rate is fairly rapid and liquid diffusion controls the crystal growth. A great diversity of these dendrite forms was produced in a single experiment, as shown in Fig. 2. Characteristic of all the crystals was a twinned structure, with twinning taking place in the plane of the two flat parallel surfaces, which were invariably (111) and $(\bar{1}\bar{1}\bar{1})$ faces. Also characteristic of nearly all of the crystals was the presence of a central core that is particularly evident in the three shown across the top of Fig. 2.

These gross features are consistent with the theory that has been put forth for dendritic growth of germanium and silicon webs,[15–20] and of platelets of diamond cubic semiconductors from dilute metal solutions.[21] It is necessary to briefly review this theory in order to understand the mechanism of growth of our crystals and how it relates to the impurity segregation that results in formation of built-in junctions. Faust and John[21] have shown that the twinned structure provides the means for extension of the crystal into the super-cooled solution. In GaP the {111} faces are the slowest growing. Without the twins a stable octahedral structure bounded by these planes would be formed and additional growth onto this structure would be difficult because of the high

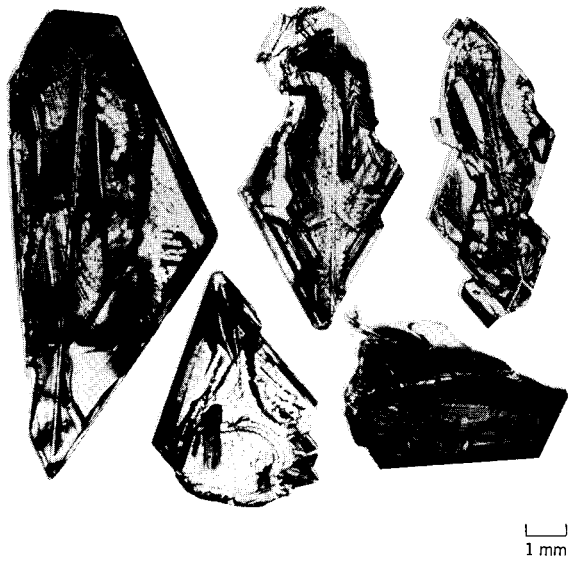
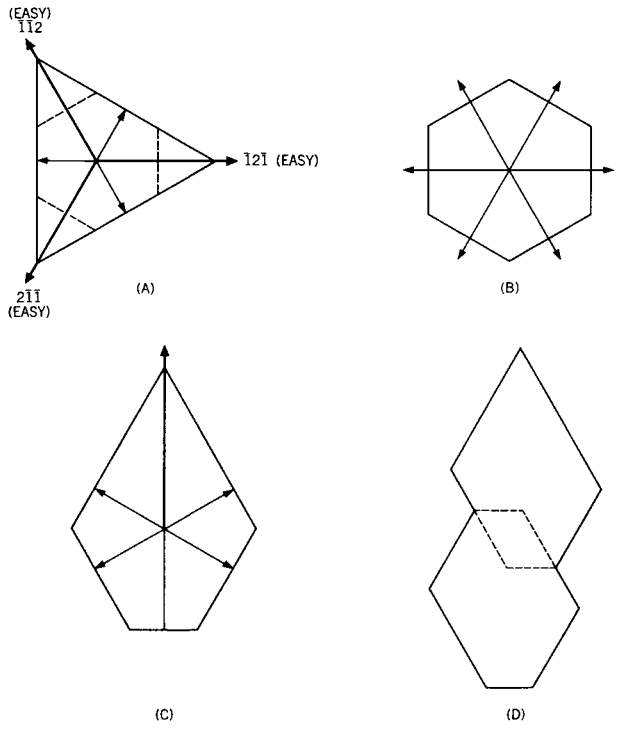


Figure 2 Typical GaP crystals grown from gallium solution.

Figure 3 Morphologies of GaP dendritic plates: (a) Odd number of twins, isotropic heat flow; (b) Even number of evenly spaced twins, isotropic heat flow; (c) Odd number of twins, directional heat flow; (d) Crystal resulting from a combination of growth mechanisms.



energy of nucleation on the flat {111} faces. In the twinned structure, however, intersection of the twins forms re-entrant grooves on alternating edges in three of the six equivalent ⟨211⟩ directions that lie in the plane of the twins. The twins intersect at ridges on the other three edges. The grooves provide locations for multiple attachment of new atoms so the energy of nucleation is lowered and growth can ensue preferentially in those directions. Whether a platelet would be expected to assume a hexagonal or triangular configuration depends on whether there is an even or odd number of twin planes; i.e., whether all edges have the same number of grooves or whether three alternate edges have more than the remaining three. In actual practice these equilibrium configurations are seldom found, for the form of the crystals is strongly influenced by the thermal gradients in the melt, which encourage growth in certain favorably oriented directions. These growth possibilities are illustrated in Fig. 3. The platelets of Fig. 2 are principally of types C and D. In a given experiment possibly 90 percent of the crystals were of these types. There were always some crystals of type A, however. These were invariably very small; probably they were formed in the center of the capsule where heat extraction was more or less isotropic.

The origin of the central core that is found in most of the dendritic crystals is also included in the theory of dendritic growth.[15] It is a consequence of the lateral growth of the crystal that begins just behind the advancing tip as layer growth that is nucleated in grooves formed at the intersection of the {111} edge facets. The crystal assumes an H shaped cross section, with the core becoming the bridge connecting the two flat parallel faces. This is the favored morphology that permits lateral growth, terminated by {111} faces, with the maximum transfer of heat to the remaining liquid. Prominent core formation should occur only in crystals where there has been rather strong directional heat flow. Under this condition, growth propagation is largely constrained to the direction of the thermal gradient.

- *Solute segregation and junction formation*

In the case of web growth of germanium and silicon, impurity segregation has been explained satisfactorily on the basis of the dendritic growth habit of the crystals.[17] The freezing point of the interdendritic material that is found principally between the arms of the H and that contains much of the rejected impurities is probably only fractions of a degree below that of the pure germanium or silicon. With those materials, although there is a prominent H-configuration just back of the growing tip, the final crystal is generally solid over the entire cross section and the growth pattern is clearly revealed by the impurity traces.

The situation is much less clear in the case of gallium phosphide grown from dilute gallium solutions. Here the lateral growth frequently proceeds entirely by extension of the arms of the H and the phosphorus-depleted solution between them remains liquid. A void results when this liquid gallium is subsequently removed.

The gallium itself is the principal impurity in the system, constituting 80 percent or more of the melt. The GaP crystal cannot grow until the excess gallium that is discharged at the growing interface diffuses away and is replaced by fresh nutrient solution. The solubility of gallium in solid GaP must be essentially zero since there is no evidence that non-stoichiometry can be achieved by dissolving excess gallium in the crystal, at least beyond a limit of about 10^{17} atoms cm^{-3} (see Ref. 22). In the time required for the excess gallium to diffuse away from the interface, all other impurities that do have solid solubility should essentially equilibrate between the solid and the bulk of the liquid and no pronounced segregation should occur in the region of the crystal bordering the space between the wings of the dendrites or in other places where there is geometrical constraint.

The fact that segregation of impurities and dopants nevertheless does occur during the growth of the GaP crystals is shown by the presence of internal built-in *p-n* junctions which result from non-uniform distribution of donor and acceptor atoms. Such junctions are revealed in the cleaved edges of the platelets by chemical etching in dilute aqua regia, which preferentially attacks the *p* regions, and by observing where light emission originates when the junctions are forward biased.

Figure 4a shows a mounted crystal with current passing in the forward direction. The presence of a *p-n* junction is evidenced by rectification in the current-voltage characteristic (not shown) and by light emitted in a band near the center of the crystal. The cleaved face of the same crystal without current flow, Fig. 4b, shows distinct twin lines that appear to correspond in position to the light-emitting junction.

Another crystal having distinct twin lines in the polished and etched face is shown in Fig. 5. In it, however, the light-emitting junction could definitely be identified with the etch-revealed boundary indicated by the arrow; its position bore no relation to the twin lines. From examination of a considerable number of other diodes it was concluded that in the isolated cases where the *p-n* junction appeared to correspond to the twin lines (such as in Fig. 4a) such correspondence was purely accidental.

From the direction of current flow in the diodes of Fig. 4 and 5 it was determined that the top surfaces were *n*-type and that the bottom ones were *p*-type. However, independent observations (e.g., reverse breakdown measurement across an angle-lapped edge) generally showed that the unmounted, intentionally doped crystal platelets were *n*-type on both surfaces and were *p*-type in the interior. Back-to-back junctions should be present in such crystals. Their presence was evident in some cases from the current-voltage characteristics, which showed reverse breakdown in both directions and were essentially symmetrical about the origin.

The presence of two junctions could also be demonstrated in some crystals by observing the origin of light emission. Figure 6, for example, shows two photographs of the same edge of a crystal with different directions of current flow. The light is emitted from two distinct regions

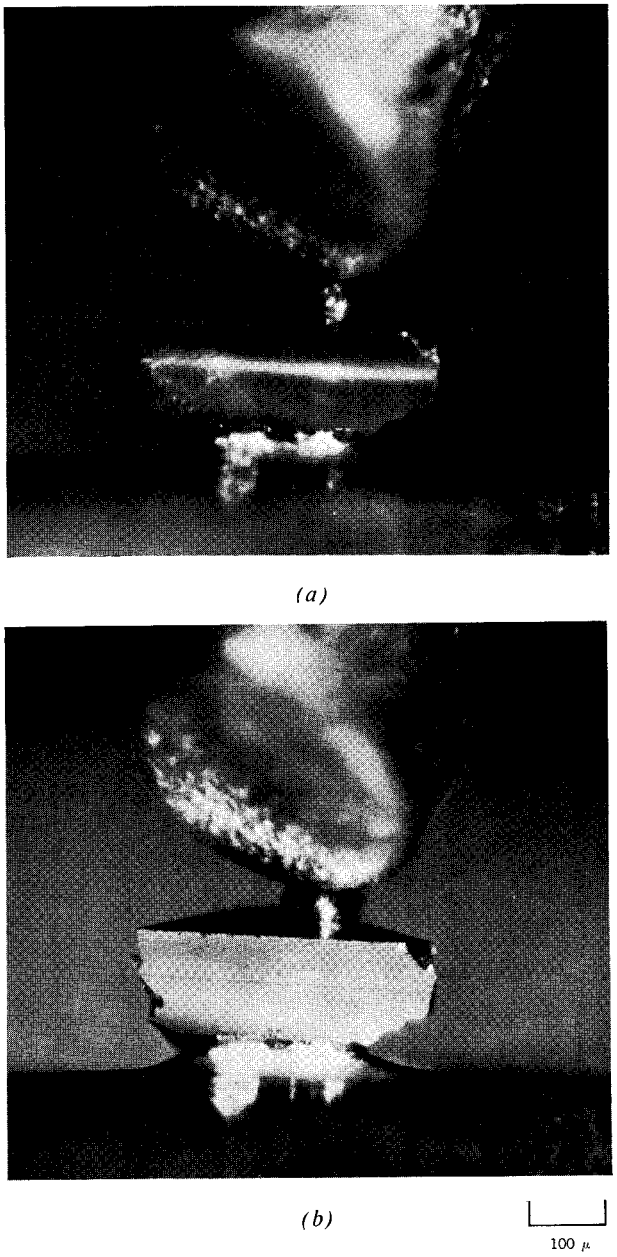


Figure 4 Photomicrograph of the edge of a GaP diode. (a) Diode on; (b) Diode off.

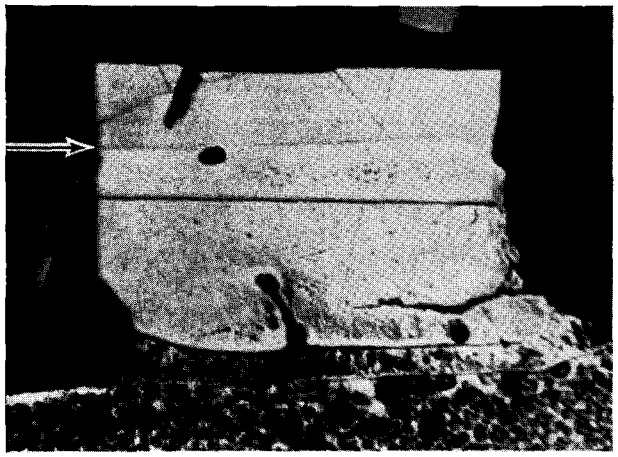


Figure 5 Photomicrograph of an etched (3HCl : 1HNO_3 : 4H_2O) section of a GaP diode. (Arrow marks the *p-n* junction delineated by the etching.)

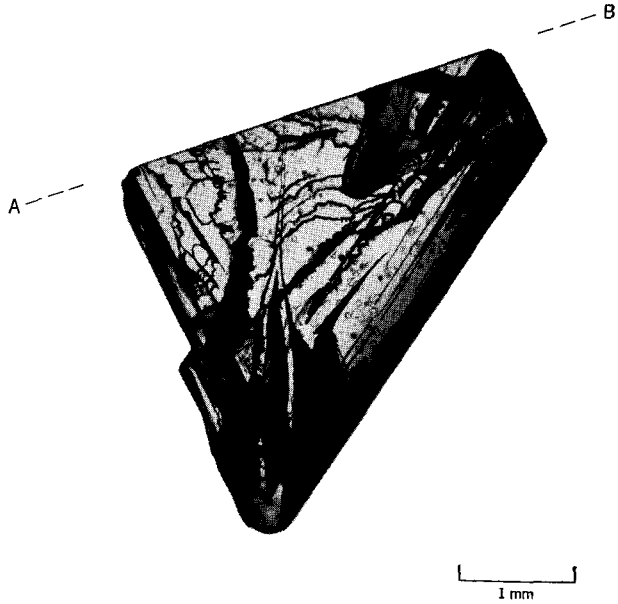
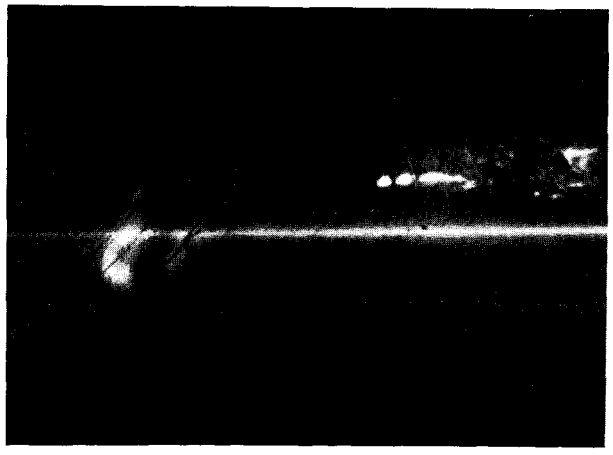
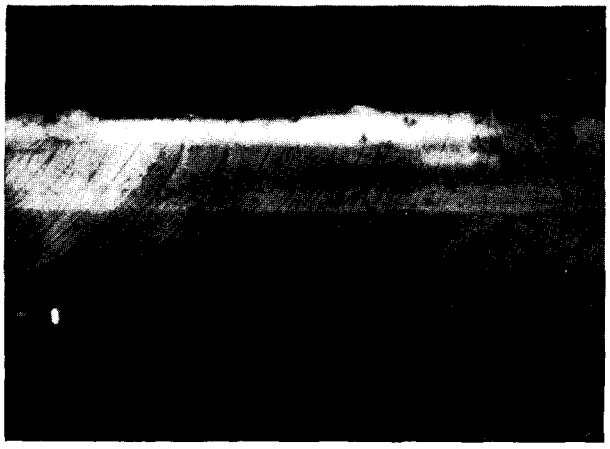


Figure 7 GaP crystal after sectioning through AB. (A photomicrograph of section AB is shown in Fig. 8).

Figure 6 Photomicrograph of the edge of a diode in (a) Forward bias; (b) Reverse bias.



(a)



(b)

depending on the polarity of the impressed voltage. Small spots of light due to microplasmas are also visible in some parts of the junctions that are in reverse bias.

When only one junction appeared to be present, as in the diode of Fig. 4, it is believed that the *n*-region on the bottom face was so thin that it was alloyed through during soldering onto the tab.*

Figure 7 shows a GaP crystal platelet that was grown from a melt doped with zinc and selenium. It was sectioned along the edge A-B; the polished and etched edge of the entire section is shown in Fig. 8. The etch that was used attacks preferentially the *p*-region, which appears as the dark gray band somewhat below the top surface of the crystal and immediately above the prominent twin lines. That the crystal morphology is typically dendritic can be judged from the shape, the twinned structure, and the presence of the core that is seen as the two parallel vertical lines at the center of the crystal of Fig. 7. If the dopant segregation that gave rise to the built-in junction occurred as a continuous process during the growth of the dendrite, the segregation pattern should have some obvious relationship to the morphology of growth as had been observed in the case of germanium and silicon dendrites.[17] However, the impurity segregation that produced the *p* region in Fig. 7 shows no interruption at the region of the core and no obvious relation to the twins or other growth features of the crystal, other than being somewhat uniformly placed below the top surface.

* It should be noted that the electrical and luminescent properties described in the companion paper pertain only to diodes showing a single junction in forward bias after contacting and mounting.

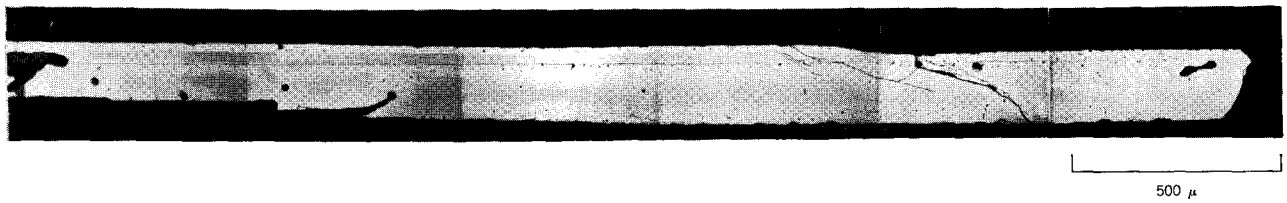


Figure 8 Composite photomicrograph of the section AB shown in Fig. 7 (section etched in 3HCl : 1HNO_3 : 4H_2O).

Figure 9 Photomicrograph of a cross-section of an undoped GaP crystal. (a) Etched in 3HCl : 1HNO_3 : 4H_2O; (b) Etched in a silver solution.

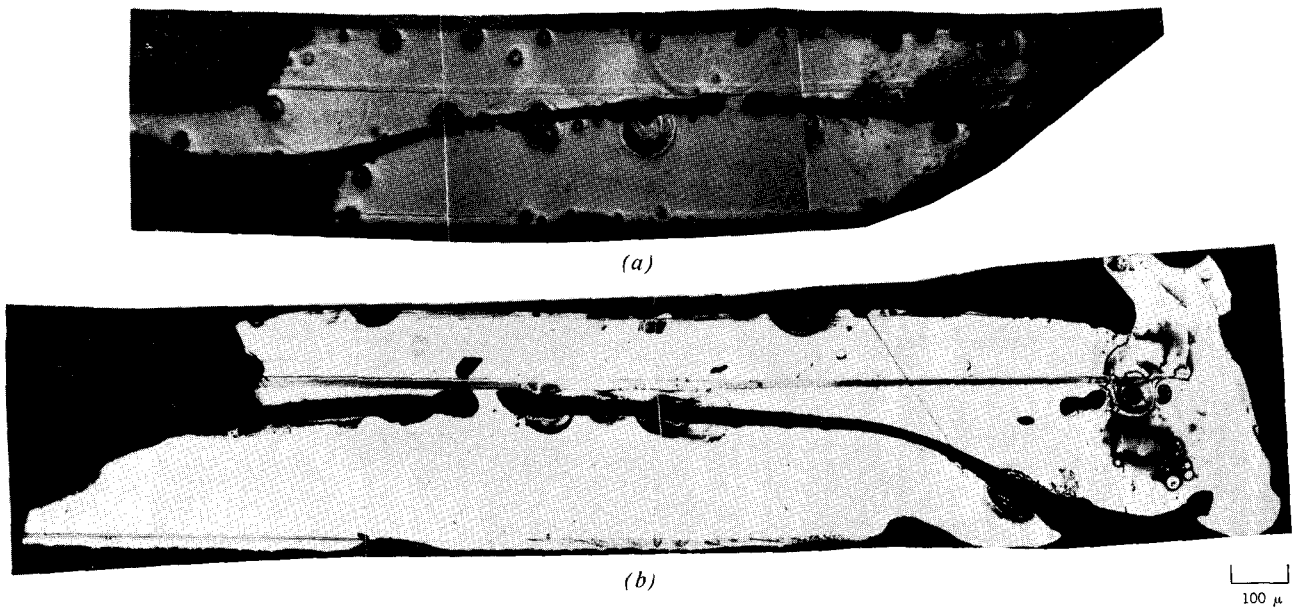


Figure 9 shows a cross section of another crystal grown from a Ga-GaP solution, but in this case without any intentional doping. The gross morphology is different from that of the specimen of Fig. 8; in particular, the space between the dendrite wings has not filled in. The specimen for Fig. 9a was etched in dilute aqua regia to show the twin lines that traverse the narrow core region horizontally. The section shown in Fig. 9b was etched in a silver solution which plates silver preferentially on *n*-type regions. This region is seen to consist of a thin, lath-like layer immediately above the narrow core. Reverse breakdown measurements on an angle-lapped edge of this crystal confirmed the fact that the central band was *n*-type and that the remainder of the crystal was *p*-type. Here again the impurity segregation that gave rise to the internal built-in junctions shows no obvious relationship to the principal dendritic growth features of the crystal. Examination of many crystals of diverse shapes, and of diodes made from them, led to the conclusion that the impurity segregation that resulted in internal junctions could not be accounted for by known growth mechanisms of dendritic crystals. Another explanation had to be found.

Experience had shown that platelet thickness constitutes the principal difference between crystals grown from rather slowly cooled Ga-GaP solutions and those grown from rapidly cooled solutions. The breadth of the platelet remained essentially constant. Thickening of the crystal by laying down of layers parallel to the twin planes is not a dendritic process but is essentially equilibrium growth that takes place after supersaturation of the solution has been largely relieved by the initial dendritic growth. Thickening is facet growth, with nucleation presumably occurring at the edge, followed by sheet growth over the (111) and/or $(\bar{1}\bar{1}\bar{1})$ surfaces. An abrupt change in impurity or dopant concentration would be expected where the growth mechanism changed from dendritic to facet. If the dendritic growth occurred

extremely rapidly, as is suggested by the observation that the platelet breadth was more or less independent of the cooling rate, the distribution coefficients of the impurities could approach unity and the dopant concentration in the part of the platelet formed at that stage would be essentially that of the melt. The dopant concentration in the overgrowth, on the other hand, would be determined by the equilibrium distribution coefficients of the dopants, since this growth is rate-limited by outdiffusion of gallium which is present in great excess and whose distribution coefficient is extremely low. Since the distribution coefficients for the donor impurities S, Se, and Te are large and that for the acceptor impurity Zn is small, the overgrowth in the intentionally doped crystals would be *n*-type, as observed.

For the *n*- and *p*- regions to be reversed, as in the case of the crystal of Fig. 9 that contained unidentified impurities, it is necessary, according to the model presented here, that the concentration of donor atoms be greater than that of acceptor atoms in the melt, and that the distribution coefficient for the acceptor be greater than that of the donor. Carbon, silicon, oxygen, and sulfur are thought to be the principal trace impurities in as-prepared, undoped GaP. It is not presently known whether any of these impurities have the necessary characteristics to be responsible for the junctions found in the crystal of Fig. 9.

Thickening of the crystal was not symmetrical about the twin planes. In all cases where the examination was made, the most flat and smooth surface of the platelet was the Ga {111} face.* The dendritic part of the platelet (that is, the internal layer that precipitated rapidly) was generally off-center and situated closer to the gallium side of the platelet. This condition requires that the equilibrium overgrowth occur more favorably on the P {111} face. The fact that this side was generally rough indicates that nucleation was easier on that face and the tendency to form a broad flat surface was less.

In summary, the growth of dendritic GaP crystals containing built-in junctions is thought to proceed as follows: The Ga-GaP solution supercools substantially below the liquidus temperature as the capsule is lowered out of the hot furnace. Once nucleation is achieved, a flat dendrite bounded by {111} faces grows very rapidly into the super-saturated liquid until sufficient heat is evolved to relieve the supersaturation. During this rapid growth, dopants are incorporated in the dendrite to essentially the same degree that they are present in the melt.

* The notation used in this paper to denote polarity is as follows: The Ga {111} is the (111), ($\bar{1}\bar{1}$1), ($\bar{1}$1$\bar{1}$) and (1$\bar{1}\bar{1}$) and the P {111} is the ($\bar{1}\bar{1}\bar{1}$), ($\bar{1}$11), (1$\bar{1}$1), and (11$\bar{1}$).

The thickening of the platelet that occurs as the melt is cooled further results from an equilibrium overgrowth onto the faces and edges of the dendrite. The concentration of dopants in this material is determined by their equilibrium distribution coefficients between the solid and remaining melt. The electrical type of the dendrite and the overgrowth depends on both the initial composition of the melt and the relative solubilities of the dopants in the GaP.

Acknowledgments

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References

1. G. A. Wolff, R. A. Hebert, and J. P. Broder, *Phys. Rev.* 100, 1144 (1955).
2. D. B. Hold, G. F. Alfrey, and C. S. Wiggins, *Nature* 181, 109 (1958).
3. E. E. Loebner and E. W. Porr, *Phys. Rev. Letts.* 3, 23 (1959).
4. H. G. Grimmeiss and H. Koelmans, *Philips Res. Reports* 15, 290 (1960).
5. J. W. Allen and P. E. Gibbons, *J. Electronics and Controls* 7, 518 (1959).
6. M. Gershenzon and R. M. Mikulyak, *J. Appl. Phys.* 32, 1338 (1961).
7. O. G. Folberth and F. Oswald, *Z. Naturforsch.* 9a, 1050 (1954).
8. M. Gershenzon, R. M. Mikulyak, R. A. Logan, and P. W. Foy, *Solid State Electronics* 7, 113 (1964).
9. D. Richman, *J. Phys. Chem. Solids* 24, 1131 (1963).
10. C. J. Frosch and L. Derik, *J. Electrochem. Soc.* 108, 251 (1961).
11. G. A. Wolff, P. H. Keck, and J. D. Broder, *Phys. Rev.* 94, 753 (1954).
12. H. G. Grimmeiss and H. Scholz, *Phys. Rev. Letts.* 8, 233 (1964).
13. R. W. Keyes, private communication.
14. D. G. Thomas, M. Gershenzon, and F. A. Trumbore, *Phys. Rev.* 133, A269 (1964).
15. G. F. Bolling and W. A. Tiller, "Metallurgy of Elemental and Compound Semiconductors," Metallurgical Society Conferences, Vol. 12, (1960), p. 97.
16. H. F. John and J. W. Faust, Jr., *ibid.*, p. 127.
17. S. O'Hara, *ibid.*, p. 149.
18. P. J. Holmes, *ibid.*, p. 161.
19. R. S. Wagner, *ibid.*, p. 171.
20. D. C. Jillson and R. E. Hysell, *ibid.*, p. 187.
21. J. W. Faust, Jr. and H. F. John, *J. Phys. Chem. Solids* 25, 1407 (1964).
22. J. F. Woods, private communication.

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