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LIGHT-EMITTING DIODES FOR LASER PUMPING

Harvey V. Winston

Hughes Aircraft Company

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July 1972

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HARVEY V. WINSTON

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LIGHT-EMITTING DIODES . R LASER PUMPING SUMMARY

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This report reviews the published literature on the application of lightemitting diodes to the pumping of solid-state laser rods. Because of the requirement of matching the LED output to the absorption bands of the active laser impurity ions, most work in this field has concentrated on the ternary alloy LEDs such as $GaAs_{1-x}P_x$ and $Ga_{1-x}Al_xAs$, which can be tuned by their composition. These alloy systems have been actively developed in connection with visible display applications, and the laser pumping application has benefited from advances in this technology. Successful operation of YAG:Nd3+ lasers pumped by GaAs , P diode arrays has been achieved; YAG:Nd3+ has absorption bands near 8100 ${\rm ilde{A}}$ which correspond to efficient emission wavelengths in both ternary alloys mentioned. For this reason, the YAG:Nd3+ appears to be the best choice for the laser to be pumped as well as for its 1.06 micron output, which is compatible with good detectors and thus suitable for many communications and ranging systems. The key to efficient operation of a diode-pumped laser is the optical and thermal design of the pumping cavity combined with a laser resonator design which optimizes the utilization of pumping light. Diodes of both alloys must be operated at junction current densities greater than 1000 A/cm2 to provide enough output power for laser pumping, and it is not known what operating lifetime can be expected. Future work on LEDs for laser pumping will probably be concentrated on achieving long operating lifetimes while maintaining the high efficiencies which are already available.

Appended to the report are data tables on the gallium aluminum arsenide and gallium arsenide-phosphide systems complete with individual bibliographies.

LIGHT-EMITTING DIODES FOR LASER PUMPING

Since the early days of solid-state lasers and p-n junction electroluminescent diodes, workers in both fields have been striving to combine the two technologies to produce efficient diode-pumped solid-state lasers. Efficient operation was expected to result from matching the narrow absorption bands of the active laser impurity ions in solid-state laser hosts. The first published work suggesting the feasibility of this approach was by Newman. Ithough he did not actually demonstrate laser action, he was able to excite the 1.06 µm fluorescence of Nd³⁺ in a CaWO₄ host by means of light emitted from selected GaAs p-n junctions. He showed that some GaAs junctions, made by partic lar fabrication techniques, emitted in the 8650-8900 Å absorption band of CaWO₄: Nd³⁺, while emission from other junctions fell cutside this band.

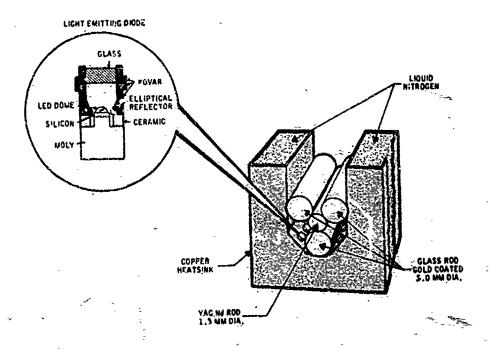
The first actual laser operation with LED (light-emitting diode) pumping was achieved by Ochs and Pankove. They employed a CaF₂:Dy²⁺ laser rod, with laser emission at 2.36 µm, pumped in its 7200 Å absorption band by a GaAs_{0.73}P_{0.27} LEP at 77°K. The laser rod operated at pumped-halium temperature, and was limited to 0.2 seconds of operation by internal heating. This work introduced the idea of adjusting the composition (and thus the bandgap) of ternary III-V LEDs to match the pumping band of the solid-state laser. About the same time, Keyes and Quist used the emission of a GaAs diode laser at 8400 Å to excite a CaF₂:U³⁺ laser line at 2.631 µm. They also suggested the possibility of using a ternary, specifically Ga_xIn_{1-x}As, to produce pump radiation around 8750 Å for exciting Nd³⁺ lasers.

In these early attempts, the principles of dicde pumping of lasers were clearly demonstrated, but practical problems also became evident. The solid-state lasers emitting in the 2-3 µm range were not desirable for many systems applications because of the lack of fast high-gain detectors. The Nd³⁺ emission at 1.05 µm is more desirable from this viewpoint, and the technology of YAG (yttrium aluminum garnet) as a Nd³⁺ host was developing rapidly. Harada and Suzuki described methods for making GaAs laser dicdes emitting around 8700 Å and suitable for pulsed pumping of Nd³⁺. Kruzhilin and Antonov also studied GaAs dicdes for pulsed laser pumping, pointing out difficulties caused by internal heating in the dicdes, including frequency shifts and changes in internal absorption. In 1968, Ross reported successful operation of a YaG:Nd³⁺

pulsed laser, pumped at 200 pulses per second by a GaAs diode laser. The GaAs output was tuned to the absorption band of Nd³⁺ at 8675 Å by cooling the diode to 170°K. It was found that the YAG rod reached threshold with 0.66 millipules of diode laser light, while 1.2 millipules of flashlamp light were required. This demonstrates the efficiency advantage of narrow-band diode output as compared to broad-band flashlamp light, an advantage further accentuated by the decreased heating of the laser rod. In the context of using laser diode emission to produce pulsed YAG:Nd³⁺ operation, Ross emphasized that many pulses from many laser diodes could be collected by the MAL rod and emitted as a giant pulse with a small beam divergence and spectral width.

A joint effort by Texas Instruments (TI) and Bell Telephone Laboratories (BTL) investigators has demonstrated actual continuous room temperature operation of a GaAs_{1-x}P_x diode-pumped YAG:Nd³⁺ laser. Their work confirms the feasibility of the concept but also spotlights the difficulties. We will review their results with particular emphasis on the LED characteristics they found necessary for laser pumping.

FIGURE I. LED PUMPED YALG: Nd LASER. (Allen and Scalise).



In the first of a series of papers describing this work, Allen and Scalise of TI reported a system in which the GaAs_{1-x}P_x LEDs were operated near 77°K. Figure 1 provides a schematic diagram of their diode-pumped YAlG:Nd laser. They employed GaAs_{0.87}P_{0.13}, which has an emission peak of 8025 Å at the operating temperature, and a linewidth between half-intensity points of 190 Å. This corresponds to the most intense absorption lines of YAG:Nd³⁺, occurring near 8100 Å. They noted that a 1% increase in phosphorus content produces a 50 Å shift toward shorter wavelength and a 1°K decrease in temperature shifts the peak 2-3 Å toward shorter wavelengths. Their system contained 15 diodes mounted on a liquid-nitrogen-cooled copper heat sink; each diode was fabricated into a hemispherical dome 0.018-in. in diameter to reduce total internal reflection, and each diode package included a gold-plated elliptical reflector. The diodes could emit 50 mW at a power efficiency of 10%. (Junction diameter was not specified in this paper; in the later related papers it was given as 0.005 in.)

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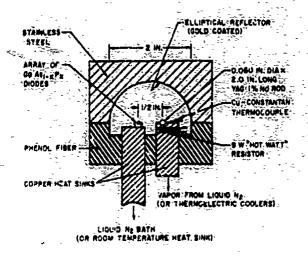
The laser output depends on the YAG:Nd³⁺ rod, the laser cavity parameters, the optical coupling between the LEDs and the rod, and the temperature of the rod. Without attempting to optimize these, Allen and Scalise obtained 40 mW output at 1.064 µm with 8W of electrical power into the LEDs, for an overall efficiency of 0.5%. There is no direct provision for cooling the laser rod in their arrangement; its temperature drops slowly toward 77°X after the heat sink for the LEDs has been cooled. At first, the rod emits at 1.0641 µm, and then another transition at 1.0614 µm starts building. After 30 minutes, only the 1.0614 µm transition survives, with no further changes. It is known that the longer wavelength is characteristic for operation near 300°K, and the shorter wavelength or operation near 77°K. The 0.5% efficiency figure is for a laser rod 1.5 x 30 mm with deposited confocal end mirrors of 99.9 and 99.6% reflectivity. The lowest threshold observed was 300 mW electrical input to the diede array, using a 1 x 30 mm rod with the same mirror reflectivities operating at 1.0614 µm.

The next step toward room temperature operation was described by Ostermayer of BTL. He used GaAs_{1-x}P_x diodes supplied by TI and apparently of the same design as those of Allen and Scalise. A major difference from the earlier TI study was the improved design of the pumping cavity, in which a linear array of LEDs as positioned at one focus of a semielliptic cylindrical reflector, with the YAG:Nd³⁺ rod at the other focus. This provided nearly theoretically maximum

optical coupling between the pump diodes and the laser rod; also the laser rod had a reflecting channel or reflecting coating covering half its surface which allowed a double pass of pumping radiation. Finall, the geometry allowed separate cooling and temperature monitoring for the diode array and the laser rod.

Ostermayer performed one experiment with LEDs operating at 77°K to determine the increase of the threshold power for YAG:Nd³⁺ with increasing laser rod temperature, achieving satisfactory agreement with a theoretical expression. The power efficiency of the 77°K diodes was 10-15%. Then, using the same laser rod and pumping cavity, Ostermayer installed a set of nineteen LEDs of the correct composition to emit 8100 Å at room temperature. These were mounted on a large copper heat sink and the whole assembly could be located precisely along the focal line of the semielliptic reflector with the help of an XYZ micropositioner and a rotating-tilting table. Figure 2 illustrates the apparatus used to perform the diode pumping experiments

FIGURE 2. APPARATUS FOR CONDUCTING DIODE PUMPING EXPERIMENTS. (Ostermayer)



A similar arrangement positioned the laser rod, which was attached to a heat sink cooled by thermoelectric coolers. With the LEDs operating at 250 mA/diode, (the maximum tolerable drive current, above which diode performance was somewhat degraded), Ostermayer determined the maximum laser rod temperature at which

threshold could be reached. With a 0.4% transmitting mirror on the laser roc the maximum temperature for threshold was -2.5°C; with both laser reflectors having high reflectivity, threshold was at 3.5°C. The room temperature LEDs were 4% efficient.

With a maximum drive current limitation on the output of each LED, a further increase in pumping power required more diodes in the linear array. Nineteen was the maximus number allowed in the 5 cm length of the pumping cavity by the dimensions of the individual LED packages in this work, but smaller packages would allow 60 or 80 diodes in the same space. Ostermayer predicted that with this arrangement it should be possible to obtain 50 mW continuously at room temperature from an LED-pumped YAG:Nd³⁺ laser.

The most recent report by Ostermayer, et al demonstrated room-temperature cw (continuous wave) operation, but only at 1.4 mW output. The paper includes a careful analysis of the effects which limit the laser output and suggestions for possible improvements. In this work, the advance which allowed room temperature operation was the increase in number of diodes in the 5 cm-long pumping cavity from 19 to 64. The individual diode elements were hemispherical domes of GaAs_{0.85}P_{0.15}, which emits near 8040 Å. The domes were 0.46 mm in diameter, with junctions 0.13 mm in diameter, on 0.71-mm square electrically inculating silicor submounts. The individual elements were mounted in linear array on a common heat sink maintained at 20°C by flowing water through it.

The peak emission wavelength and the spectral bandwidth of the array, which determine the degree of spectral matching with the YAG:Nd³⁺ pump bands, vary with diode current because of heating effects. By comparing cw las are output powers with output powers after current pulses of a few milliseconds, and by correlating changes in laser output with changes in diode emission, the authors concluded that three effects combine to give a net decrease in rumping efficiency with heating of the diode array. A shift in peak wavelength from 7920 Å at low currents to 8020 Å at 225 mA/diode improves the efficiency, but is approximately compensated by a decrease in total power output with heating. The third effect is an increase in spectral bandwidth. I the array, caused by differential shifts in the peak wavelength of different diodes according to the effectiveness of their heat sinking. The bandwidth increase causes some of the LEB output to fail outside the absorption band of the YAG:Nd³⁺. Several

time constants were observed in the decay of the laser output from its short pulse value to the cw value; a 30-msec decay was associated with heating of the diode elements with respect to the heat sink and a 20-sec decay related to heating of the heat sink. A further 160-sec decay was connected with a rise in temperature of the laser rod heat sink, though in normal operation the thermoelectric coolers on this heat sink were set to hold the temperature constant.

One of the laser rods had flat parallel ends with one high reflectivity coating and one antireflection coating, so that it could be used with an external output mirror. Varying the radius of curvature of the output mirror caused a change in the TEM_{OO} mode diameter; the larger the mode diameter the higher the threshold. This was attributed to the focusing of the GaAsP junction radiation in the YAG rod. The lowest threshold was found with another rod with a resonator configuration giving the smallest wide diameter. The authors proposed to achieve an efficiency increase in future work by using a wider diode array and a larger diameter laser rod with a larger TEM_{GO} mode. They point out that the input power goes up linearly with array width while the output power goes up as the square.

At a drive current of 225 mA/diode, corresponding to input power of 30W, the optical output of the diode array was 0.90W, for an average power efficiency of about 3%. The 1.4 mW continuous laser output at 20°C corresponds to a total power efficiency of 0.005%. However, in millisecond pulse operation, the power efficiencies were higher; 4.9 mW for a 36W electrical input, and 15.7 mW for 44W input, approaching 0.04%. The authors expect that cw operation at close to the pulsed efficiency could be realized by more uniform heat sinking of the diodes in the array. Finally they point out that with the laser rod at 0°C, the pulsed output for an input of 44W was 55mW, giving an efficiency of 0.13%. Since it requires only 2W of power to the thermoelectric coolers to maintain the laser rod at 0°C, under cw conditions an overall efficiency of 0.12% could be anticipated for these conditions, once the heat-sinking of the diodes is made uniform.

These are, until now, the highest efficiencies reported or realistically predicted for diode-pumped laser operation near room temperature. The 77°K results of Allen and Scalise corresponded to 0.5%, and this might increase several times if the more efficient pumping cavity of the later experiments

were employed. It must be noted that the drive currents for the LEDs correspond to junction current densities of about 1700 A/cm². This is much larger than the usual values, on the order of tens of A/cm², for LEDs used in the visible region.

The TI-BTL work just reviewed has demonstrated some of the practical difficulties for diode-pumped lasers, as well as providing a background for the requirements on LED pumps for this application. Briefly, the LEDs must emit light within the pumping band of the solid state laser ar a high e This limits the choice of material of the LED to those which can have their bandgap and hence emission wavelength "tuned" by varying the composition. For pumping YAG: Nd^{3+} with its pump band at 8100 Å, the present choices are the ternary alloys $GaAs_{1-x}P_x$, the material used by the TI-BTL workers, or $Ga_{1-x}Al_xAs$. These materials have received a great deal of attention for other LED applications and the technologies for preparing them and fabricating them into device structures are well-developed. The other materials which can be tailored to emit at 8100 Å, $In_{1-x}Ga_xP$ and $In_{1-x}Al_xP$, are much less advanced, but they are receiving attention for visible LED applications and should be considered as future candidates for laser pumping. Two recent reviews by Bergh and Dean and Nuese, et al. of the entire LED field have included discussions of the ternary systems, covering the theory of their operation and preparation methods, and giving extensive bibliographies. In the remainder of this report, we will draw on these review papers to summarize the design principles and preparation methods applicable to laser pumping diodes. We will also discuss recent work on Gal-xAlxAs high-efficiency LEDs suitable for laser-pumping, and comment on the limited literature on degradation and reliability.

The tunability of bandgap in the ternary semiconductor alloys of interest for laser pumping, is a consequence of the change in electronic energy band structure with composition in these materials. In each case, the bands change from the direct gap structure characteristic of GaAs, for example, and at a particular crossover composition the lowest conduction-valence band separation becomes indirect. In a direct material, the lowest conduction band state is at the same point of the Brillouin zone as the highest state of the valence band, which leads to a high probability for radiative recombination of excess holes and electrons. In indirect materials, these states are at different locations in the Brillouin zone, and radiative recombination is generally much slower,

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occurring only with the intervention of phorons or with the aid of impurity levels. Thus direct gap materials are much more efficient light emitters than the indirect ones, since competing nonradiative recombinations are less important, and this circumstance plays a central role in many LED applications, because the band gaps in the visible range are generally on the indirect side of the crossover composition. Fortunately for the YAG:Nd³⁺ laser pumping application, the required band gaps are in the direct range of composition.

The mechanism of light emission in an LED is the radiative recombination of excess current carriers injected across a forward-biased p-n junction. Direct-gap semiconductors have a high internal quantum efficiency compared to indirect-gap materials for the reason just discussed. However, because of their higher radiative transition probabilities for light at or near the bandgap, direct-gap materials may absorb, within the LED itself, the light emitted at the junction. This is a problem for the laser-pumping diodes as well as for visible range LEDs, and has occasioned the development of special configurations to minimize the internal losses. The general principle of these schemes is to provide a path for the emergence of the light generated at the junctions through material of higher bandgap and hence lower absorption. The emergence of the generated light is also hindered by dielectric reflection effects at the interface between the diode and the external medium; ordinary reflection loss is minimized by anti-reflection coatings, while total internal reflection losses are avoided by using dome-like structures, so that the light is traveling nearly normal to the interface when it reaches the surface of the diode.

Electrical losses in the diode structure are kept low by maintaining a low diode series resistance by means of high doping levels and favorable geometrical design.

The details of the fabrication of the GaAs_{1-x}P_x LEDs used in the TI-BTL laser pumping work were not given in the publications. However, GaAs_{1-x}P_x diodes are usually fabricated by vapor-phase epitaxy. Suitable goseous mixtures of arsenic and phosphorus (formed by the thermal decomposition of arsine and phosphine) with a gallium-chlorine compound (formed by passing Holl gas over molten gallium) react to form the ternary alloy as a deposit on a GaAs substrate. Dopants can be introduced in gaseous form at various times during the apposition or subsequently by diffusion. The process is very flexible, allowing precise control of the composition of the deposited layers through the flow rates of

the gaseous reactants. The basic process has been used commercially for several years, and is well adapted to volume production. It is usually necessary to grade the composition of the epitaxial deposit from pure GaAs to the desired composition of $GaAs_{1-x}P_x$ (by varying As/P ratio during the growth) in order to avoid the effects of lattice mismatch.

Liquid-phase epitaxy is the preferred growth method for $Ga_{1-x}Al_xAs$. The material is grown from a melt of gallium, gallium arsenide, and aluminum onto a substrate of gallium arsenide or sometimes gallium phosphide. Many refinements in the technique are available; some are discussed by Blum and Shih. The method has been particularly well developed in connection with the fabrication of heterostructure $GaAs = Al_xGa_{1-x}As$ laser diodes; a recent paper by Miller et al. describes a method to obtain high uniformity and reproducibility.

Reflecting the less advanced state of $Ga_{1-x}Al_xAs$ LED technology compared to that of $GaAs_{1-x}P_x$, there have been no reports of laser pumping with $Ga_{1-x}Al_xAs$ LEDs. However, several recent papers contain discussions of highly efficient laboratory diodes or of configurations which might be adapted for laser pumping.

Dierschke, Stone and Haisty have produced $Ga_{1-x}Al_xAs$ Zn-diffused LEDs emitting at 8150 Å. The power efficiency at maximum cutput at 25°C was 12%. The high efficiency is the result of a grading of the alloy composition so that light emitted at the junction emerges through material of higher bandgap than the junction itself. In their process, the ternary is grown on a GaAs substrate; because of the high distribution coefficient of aluminum in favor of the solid ternary, the melt is depleted of aluminum and the bandgap of the epitaxially deposited material decreases away from the substrate. The deposited layers are 0.03 to 0.06 cm thick and doped n-type by tellurium from the melt. The next step is the formation of a 0.011 cm p-n junction by zinc diffusion on the side away from the substrate. Then the GaAs substrate is removed and the units are formed into hemispherical domes. An anti-reflection coating of SiO is applied to the hemispherical surface and electrical contacts to the n and p regions on the plane surface of the hemisphere are made by means of metallization patterns on a silicon submount. The reported spectral bandwidths of the emitted light range from 250 to 670 Å, which indicates that in some cases light will fail to match the YAG:Nd³⁺ pump band. The authors ascribe the wide bandwidths to location of the junction in regions with too high a composition gradient; since some units already have low bandwidth it may be expected that improved

control of the fabrication process will generally yield acceptable bandwidths.

Woodall et al have produced LED structures starting with a GaP substrate. The high bandgap of the substrate allows it to be included in the finished device without absorbing the junction light, and the layer of Ga, Al, As need not be so thick that it can survive separation from the substrate. In this work a four-malt system was employed for the liquid epitaxy; the substrate could be moved from melt to melt with or without losing the solid-liquid interface, and counterdoping of each melt during growth was possible. Phosphorus contamination arising from meltback of the GaP substrate in the first melt was greatly reduced by moving the substrate and the initial deposit to the next melt. Other melts allowed changes in the composition in addition to those caused by depletion of aluminum in the melt. In one structure, the composition was graded approximately linearly from the substrate to the junction. Each melt contained tellurium for n-type doping; the junction was formed by counterdoping the third melt with zinc during growth. A test device was formed into a mesa structure to allow contacts to both n and p regions on the same side. This diode emitted at 8500 Å with an external quantum efficiency of 1.2%. A similar structure with a roughly hemispherical dome formed in the GaP substrate had a quantum efficiency of 5.5%. An even more promising result was obtained with a structure in which the light was emitted in a region grown from a melt much less rich in aluminum than the other melts. This "minimum bandgap" structure is really a heterojunction device, since the junction is between a p-region of one composition and an n-region of another composition. A mesa diode of this type emitted at 8000 Å with 3% efficiency; presumably a dome configuration in the GaP substrate would increase this by something like the (5.5/1.2) ratio for the linearly graded device. Despite the observation of many metallurgical imperfections in these structures, they apparently do not affect the electroluminescent behavior of the active layers.

Burrus and Miller have described LEDs based on $\operatorname{Ga}_{1-x}\operatorname{Al}_x\operatorname{As}$ designed to couple efficiently to optical fibers. They deposited successively on an n-type GaAs substrate n-type $\operatorname{Ga}_{1-x}\operatorname{Al}_x\operatorname{As}$, an emitting layer of p-type $\operatorname{Ga}_{1-y}\operatorname{Al}_y\operatorname{As}$ (y less than x to make this the lowest bandgap region), p-type $\operatorname{Ga}_{1-x}\operatorname{Al}_x\operatorname{As}$, and p-type GaAs for contacting purposes. A 50 µm diameter contact dot was defined on the last GaAs layer, and the GaAs substrate was etched away above the dot so that it would not absorb the light emitted by the active layer. In this application, a clad optical fiber was attached by epoxy resin to the window

報題の表現的情報を開発していませんのないのできませんのできました。 は、 Total Andrews etched in the substrate. The light output near 8000 Å from a 30-cm length of fiber with an input current of 150 mA was as large as 1.7 mW. It may be interesting in the future to consider arrays of such units in which the emitted light is brought to a laser rod via optical fibers, eliminating the usual pumping cavity and to some extent allowing the LEDs to be geometrically and thermally decoupled from each other.

Like all semiconductor devices, LEDs are likely to suffer a change in characteristics, usually for the worse, during operation. Long operating life without excessive degradation of light output and efficiency is essential for the laser-pumping application of LEDs. The published ampirical information on the degradation of units suitable for laser pumping is neither extensive nor conclusive at this time. Galanda, As emitters were lifetested by Dierschke, et al. at 25°C under a current density of 1500 A/cm²; after 5000 hours the best ones had degraded less than 15%. The Galanda, As sources of Burrus and Miller were reported to have operating lives to half-output at 7500 A/cm² of at least several thousand hours. Double heterostructure laser diodes having a related structure have not yet achieved long operating lifetimes; Miller et al. report very substantial degradation after 25 hours of room temperature cw operation.

LEDs for visible display applications exhibit operating lives of many thousands of hours. Hartman et al. have given the most optimistic estimate of half-life for LEDs of 10⁸-10⁹ hours at room temperature. This is for GaP units specially passivated to prevent the introduction of impurities. Of course, visible LEDs are operated in the range of tens of A/cm², while the laser pumping diodes (at least those proposed so far) all require bias current densities above 1000 A/cm². Thus the operating conditions are much less favorable for long life for the laser pumps. There is some hope that degradation may be at least partially reversible. Burrus and bawson, working with high current density GaAs light emitters found that applications of a periodic reverse bias with a duty cycle as low as 1%, slowed the degradation dramatically, and further, a previously degraded diode could be restored by heating at 100°-200°C, under zero or reverse bias for several hours to a few days. Possibly laser pumping is compatible with degradation-delaying bias schedules of this kind.

There is general agreement that the degradation of LEDs arises from bulk effects near the p-n junction. Schade, Nuese, and Gannon have provided direct

evidence that non-radiative defect centers do appear near the junction in GaAs_{l-x}P_x diodes which have undergone degradation. Their measurement of thermally stimulated currents showed a greater number of centers in the more seriously degraded devices. Their results could not identify the defects, however, beyond assigning energy levels to them. The degradations were from 5 to 50% after 2000 hours of operation at 10 A/cm². Centers could have been formed by the Longini mechanism (the transport of charged interstitial impurities across a p-n junction into a region where they complex or precipitate) or by the Gold-Weisberg mechanism in which some of the energy liberated in nonradiative recombination generates vacancy-interstitial pairs. If the nonradiative recombination takes place at an impurity atom, the interstitial can be the impurity itself.

Bergh, working with GaP LEDs, showed that intentional introduction of copper accelerates degradation and careful elimination of contamination by copper and similar impurities greatly increased diode life. He concluded that the mechanisms of degradation, whatever they might be, were not inherent in the operation of the device. It remains an open question whether degradation can be sufficiently reduced in the ternary LEDs to make the laser pumping application really practical.

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APPENDIX

1

Gallium-Aluminum-Arsenic and Gallium-Arsenic-Phosphorus Systems Data Tables

M. NEUBERGER

These Data Tables provide the most reliable information available for the physical, crystallographic, mechanical, thermal, electronic, magnetic and optical properties of $Ga_{x}Al_{1-x}As$ and $GaP_{x}As_{1-x}$. All data points are referenced. Where two or more documents present the same data values, all are cited. The bibliography which follows each of the data tables is arranged alphabetically by author; more than one document by the same author is distinguished by the letters A, B, C, etc.

Other III-V ternary systems for which data are available are included in "Handbook of Electronic Materials," Volume 7, III-V Semiconducting Compounds, Data Tables which is to be published by Plenum Press during 1972.

GALLIUM-ALUHINUM-ARSENIC SYSTEM

PROPE! TY	SYMBOL	. VAL	VALUE UNIT		NOTES	TEMP.(°K)	REFFERENCES
Formula		Ga×A1	-x ^{As}				•
Density		<u>x</u>	g/cm ³		Alās	306	D
		34 42 95	4.29 4.40 5.24		closed tube, iodine vapor transport, single crystals deposited on high purity, (110) GaAs		Donnay Black & Ku
		200	5.307		SaAs		Bateman et ai.
Color		10 20 60 70 80	orange red-ora red reddish		transmitted white light through apitaxial, CVD thin films on alimina the thick	:	Manasevit, Bindeman et al.
Symmetry		eub	ic				
Lattice Parameter	· a c	o	a _o (Å) 5,6605		Alas		Ettenbarg &
		42	5.6581				Paff Black & Ku
		100	5.65191		GaAs		Cooper
Thermal Expansion	Coeff.	9	5,20	10 ⁻⁶ /~c	AlAs, linear from 20-1000°C, lattice match AlAs-GaAs at 800-1000°C complete	20°C	Ettauberg & Paff
		190	0.86		GaAs		Pierron et al.
		At. % of					
Liquidus Isotherm	s	3a A1 96.5 1.0 94.0 1.0 89.0 1.0 94.0 1.0 92.5 5.0 95.0 5.0 82.5 15.0	As 2.5 5.0 10.0 15.0 2.5 5.0 10.0 2.5	898 952 1037 1082 1202 1067 1140	first solid for slow cooling of high gallium solutions		Panish & Sumski, Ilegems & Pearson (B;
Dielectric Constant Optical	nt E _{us}	× 96-99.	5. 5 11.0		cotical meas.	300	Sikharulidze
		18	8.5		n-type, polycrystalline reflectivity meas. on single crystals	300	et al. Ilegens & Pearson (A)
Effective Mass Electron	n _n		(10 ¹⁸ cm ^{-:}	3)			•
		90 0.071 94 3.674 96.5 0.070 99.6 0.064	1.32 1.60 1.63 1.80		reflectivity meas. on n-type, polycrystalline material, 30p thick	300	Sikharulidze et al.

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PROPERT /	:	Symboi.		VAL	UΣ		UNIT	7		NOTES	TEMP.(°K)	REFERENCES
Energy Gap		Eg	×	Eader	15-r ₁)	E., (1	Γ ₁₅ -γ ₁)				
Direct Indirect		E _{gd} E _{gi}	0		.90	-	2.13	eV		AlAs		Kischio, Lorenz et al.
-			25 34 48 55 68 85	2 2 2 1	.42 .30 .32 .0 .82	:	2.0 1.95 1.86 1.85		-	barrier consé reas.	309	Casny & Panish
			100	1	.4257					JaA s	300	Zvara
Energy Banc Structure				E _{nd}	E _{g1}	<u>F</u> 1	E, -					
			53 57 75 80 83 87.5	1.97 1.81 1.67	1.94	3.15 3.06 2.95 2.96 2.96	6 3. 7 3. 5 3. 3 3.	.33 eV .27 .16 .14 .14	prepar crysta	clar beam. vapo vation, single cl films, ctivity meas.	r 300	Cho & Stokowsk
	×	Eo	E _c +A	o E	ı E,	+41	Ec,	E . + 40	E2			
	0 25 34 48 55 68 85	2.93 2.49 2.36 2.16 2.04 1.80 1.63	2.95 2.54 2.39 2.06 1.66	3. 3. 3. 3.	4 3 25 3 2 3	.7 .6 .5 .4	4.7	4.75 4.75 4.7 4.6 4.6	4.85 4.85 4.9 4.9 5.0	AlAs electroreflec tance meas. o LFE deposited 1 mil thick 1 on GaAs GaAs	n •	Berolo & Woolley
Direct-Indir Cross-over		2.76		×	1.92 eV		~.~	4.0		oluminescence	300	Dierschke
				65	1.92					oluminescence	300	Berolo & Woolley
Phonon Branc	h Speci	tra	×	ಬ್ಬ	Lu ₂	то	, 1					
Longitudin Tr e nsverse		TO	47	49.60 49.60 47.87 47.61 47.10 46.75 46.36 44.89 44.63	31.98 33.48 34.46 35.46 35.71 35.96 36.02 36.08 36.21	44, 45, 44, 43, 44, 44,	.89 .25 .89 .63 .65 .15 .15 .3 .15 .3	~ meV 31.74 31.74 31.98 32.24 32.37 32.49 32.49 32.37 33.11		civity meas. gle crystals	306	Ilegems & Pearson (A)
Refractive I	ndex	<u>د</u> ۳.		×	n					•		6.5
			-	12	2.9					tivity meas.	300	Ilegems & Pearson (A)
				90	3.3					l meas. on crystals	300	Sikharulidze et al.

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GALLEUM-ALUMIN'M-ARSENIC SYSTEM

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PROPERTY	S!MBOL	v	ALUE	U	NIT	пол	res temp.	(°K)	REFERENCES	
Electron Emission (Cold Cathode)	×	Wavelength (%)	Emis Current (A/c	Density	Efficiency (%)	Photo- sensitivity (uA/lm)	•			
	89	8700-8800	0.	1	4.0	de	LPE- 30 eposited on oped GaAs, s ₂ 0-covered	06	Schade et al. (A, B)	
Use in a P.H. Junction Laser	X	Wavelength (A)	TCP A/qm²	Efficien (%)	lv lower Output					
	75	8700	5x10 ³	46-47	560 mM	dcuble ture je LPE, st GaAs, r i)n-, Sn- i)n-, p-, 3)p-, Ge- 4)p-, Ce- layers	7			
		3460 9130	24 1100	50	-	hetero	optical cavity junction lase: 400u long, 2:	•	Kreseel et al.	
			3600 2000		0.04 W 1.2 W		uous wave oper operation	y. 93 0		
	60-8 94	G 357E 8540	1000 2500	30-40	29 mW	ture Li continu	heterostruc- PE injection : uous operation rolarized ligi	laser, ni	Hayashi et al.	
Electroluminescent	: x	Wavelength (A)	Current Pensity		ower utput		-			
Quantur Efficiency	n	8150 6950	360 mA	-	Wm 03	LPE de	fused diodes, posited on Gau junction dep		Dierschke et al.	
		6700		0.3 4.0			posited on Ga. type layers, hick	As 300 77	Beceking et 41.	
		9 3¢9					n implantation doped CaAs, hick	77	l insperger 6 Yarsh	
		6700-7000				anneal	ed 5 hr. at	77	•	
			TCD ∆∕em²	Efficienc	: Luminance			•		
	62-5	7 6550,	40	0.23	164 ft L		posited p-n on, 3-7p thic	300 k	Shih & Blum	
					Power		*			
	70	7756-7340	7500	•	1.7 mH	ture. diode multim	heterograuc- to tick, coupled to ode options for our operating	ibors,	Burrus & Miller	
	10	5760 (stro	ng)			crysta	ed single ls. photo- soffce meas.	4.2	B'ndemann et al.	
Light Modulation			Phuse Modulat	Bias ion Volts					-	
	75	11533	1600	1C /	/ 0.1 mW/1	MHz 1 mm 1	eng^t di∞de	300	Reinhart 6 Miller	

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一個年代中國語 人名英格兰人姓氏 人名西班牙克 医二种种

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GALLIUM-ARSENIC-PHOSPHORUS SYSTEM

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				galliup-ars.	ENIC-PHOSP	HORUS SYSTEM		
ROPERTY	SYMBO	i,	IAV	NE	CHIT	NOTES	TEMP.	(°K) REFERENCES
ormula			GaP _x As	1-x				
ensity		×	GA	gin (gr/	<u>ce³)</u>		-	
)3	5.20	5.32	**************************************	GaAs	293	#Jones et al. ##Abagyan et al.
		38 58	4.6E					
		66	4.62 4.57					
		72 74	4.51	4.48				
		78 92	 	4.42 4.23-4.36		O-D		
		100	4,14	4.16		GaP		
olor		yel:	low to dan	ek cherry re	d	transperent, v. transport prep of elongated t	aration	Abagyan et al.
attice Parameters	40	×	Jones	Rubenstein	Cooper	Fierron et al.	Abagyan et al	<u>.</u>
			vapor epitaxy single or.	single or. I-vapor transport		I-vapor trensport	ges-transport single cr.	-
		Q	5.65332 (calc.)	5.6532	5.64191		5.6527	GaAs
		10 13	5.618	5.6305				
		20 30		5.6103 5.5890				
		38 40	5.578	5.5676				
		41 50		5.5483	_	5.5567 5.5565		
			5.550		-		5.5624	
			5.538 5.510	5.5296		•		
		70 72 74	5.503	5,5094			5.501	-
		78 98		5,4994			5.499	
		30 30		5.4704			5.473-5.482	
		100	5.4505	5.4505		5.4495	5,450\$	SaP
elting Point	м. Р		<u>×</u>	M.P. 1238	90	GaAs		Richman
			5 15	127,				Osamura & Murakami,
			15 45 50	12°C 1°25 1'50				Antypes, Osamura et el.
			55 73	.360 .360				одиники бір бірі
			90	1-20				
			100	1467	۰.	GaP		Pichman
Thermal Expansion (oeff.		9 41	5.41	10-5 /sp	GaAs from lattice o	constant meas.	Pierron et al.
			50 190	5.91 5.81		Gal		
						-		

GALLIUM-ARGENIC-PHOSPHORUS SYSTEM

PROPERTY	SYMBO!	VÁLUE	UNIT	HOTES TEMP. (*)	K) REFERÊNÇEL
Thermal	*	* k(½/cm °k) 39°k 273°k 10 1 0.22 20 - 0.20 33-35 0.4 0.18 50 0.27 0.14		polycrystalline, Te- Se- and Si-doped n _n = 2-4×10 ¹⁸	Carlso. e'
Dielectric Constant Optical	£ #4	579K 3009K J 10.4944 10.7479 6 19.3710 10.6314 17.5 19.2313 10.4601 25 10.0866 19.2909 35 2.9871 10.1632 41.7 9.8382 19.0331 62.5 9.5607 9.5203 190 8.8599 8.4980		GaAs single crystals grown by closed tube, iodine vapor transport method; optical meas. in infrared GaP	Clark & Holonyak
~		6 10.76 28 10.20 56 9.53 65 8.86 99 8.45	[™] -ge-	optical reflectivity meas. $_{\rm R}<$ 10 16 cm $^{-3}$	Varleur & Barker
Mobility Electron	μn	x ν _n (cm²/V sec) 38 3150		Ges transport, vapor 300 phase, epitaxial, single crystals, n = 1.5x10 ¹⁵	Ogirima & Kurata
		170K ^u n 300°K 3-33 15000 5000 40 1300 70 500		epitaxial vapor deposition on (100) GaAs, not doped, n= 5x10 ¹⁵ -10 ¹⁶	Tietjen • Weisberg
	1 1 2 3	0 GaAs 5000 L 5 - L 10 5000 L	0000 0000 0000 0000 0000 0000	epitexial, n-type, single 300 crystal, closed cube, vapor deposition on (110) GaAs or GaP, indine transport, Se, Te or Sn-doped	Ku
	2 2 3 4	12 1580 80 900 85 700 84 400 85 100	1.0 1.6 0.3	epitaxial, n-type, single 300 crystal, vapor deposition, Se and Te doped	Wolfe et al.
	7 8 8 8	Un (Tr ² /V sec) Dopant 175° × 300° × Dopant 170 160 85 Te 180 190 90 Te 180 190 70 Te 180 150 90 Se 180 200 100 -	1.9 2.1 1.3 5.3 2.4 0.4	cm ⁻³) single cryetels	Yurova et al.

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Effective Mass Electron	²⁵ n	-	× 	^m n 9.085		^m o				300	Hill.
Composition Coeff	F,		r n	0.072				-			Craford et al.
		20 25 30 55 72	3.32 0.15 0.18 0.47 5.47		.5 .5)	and f	ara 245	reflectivity day rotation on n-type	306	iglitsyn et al.
Energy Band Structure	×	E	49 .	E ₂	۵ ₁	E _o '	£2				
Direct Gap, E _o Spin-Orbit A _o Splitting	3 10 20 30 45 56 66 73 80 97	1.43 1.55 1.67 1.92 1.90 2.04 2.16 2.29 2.60 2.75	0.33 6.32 0.28 0.27 0.25 0.19 0.18 0.16 0.12 0.09	2.90 2.94 3.01 3.06 3.14 3.27 3.38 3.41 3.58 3.66	6.23 6.24 9.22 6.23 6.23 0.21 6.19	4.46 4.48 4.52 4.52 4.58 4.61 4.63 4.67	5.01 5.03 5.04 5.13 5.17 5.21 5.24 5.28	eV	GaAs electroreflec- rivity meac., sealed tube, iodina transpor polycrystalline n= 10 ¹⁷ ; GaAs a GaP are single crystals	١,	Thospson et al., Irzikevizius et el.
	29		5.339	3.003	0.232	4.61			electroreflec- tance meas.	300	Rehn
	20		°, 021	3.053						180	Rehn
	28 43 47 70 78		0.275 0.242 0.230 0.190 0.170 0.250	· · · · · ·					optical meas, c single crystal, epitaxial films	,	Hodby, Belle et al.
Indirect Gap E		* K		i(eV) itzer &	Koad						·
		30 1 40 50 2	.85 .90	1.65			Copos	ite	meas. on 1-vapor 1. single orystê 1 films		Ku
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PROPERTY	SYMBOL	٧	ALUE	CI	VIT	NOTES	TEMP. (°K)	REFERENCES
Magnetic Susceptibility	X mol	9 30 45 71 75 100	32 36 28 28 27 27	10-6	cgs	GaAs single crystal, no 10 ¹⁷ Faraday rotation meas. at 77-300°K GaP	300	Andrienov et al.
Refractive Index	25 25 25 35 41.7 62.5 100		4 35 31 3.45 28 3.40 25 3.37 20 3.30	3.47 3.28	2.67; 3.33 3.30 3.26 3.24 3.19 3.14	3.47 cl 3.45 ha 3.41 tr 3.35 3.52 po 3.33 3.47 Se	osed tube, logen vapor ansport, lycrystals, - or Te-dope: 1010	Clark & Holonyak
Photoemission Quantum Yield #(slectrons/quant	.mw)	× 25 3		length A) 000		cesium activated	300	Simon et el-
		30 70 100	0.10 6 0.25 5 0.01 5 0.20 4 0.19 4	030 000 000 000 133 103		p-type photocathode cesium coated, Zn-doped closed tube, iodine vapor transport crystal		Garbe
Diode Properties Brightness B	*	B(fL)	Wavelength (A)	<u>(\$)</u> (CD <u>A/cm²</u>)	,		
Quantum Efficienc Current Pensity	y 5 40 29	720	6520	0.2 6.6	4.4 4.4	<pre>In-diffused, vapor grown, epitaxial films, no 10¹⁶-10¹⁷</pre>	300	Herzog et al.
	38		9500	0.2	0.58	2×1016	300	Ogirima 6 Kurata
	40	1000	6450		10	vapor grown, 1017-1618	30 0	Burgeister et al.
	40	max.	6533	0.06	10	n~10 ¹⁷ , relenium doped epitaxial layers, cathodoluminescence mass. 1.2-1.5µ junc- tion depth	300	Heath & Stewart
	75	200	5850	G.002	16	Zn-diffused, vapor grown, epitaxial diode, 5.5x1016, 0.3-0.4 mm ² a		Epstein & Huebner
	45	450-650 (at 10 A/c	6649 m²)	3.E 0.2	20	Zn-N doped Zn-doped, vapor phase, epitaxial EL diodes	300	Groves et al.
	34-37			2,75 5.21		EL díodes n°- 4x10 ¹⁷	75 300	Maruska & Pankove
	28 42	>300 8560	6600 6600	0. 03 5	10	vapor grown EL diodes	300	Nuese et al. (A, B)

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PROPERTY	SYMBOL		VALUE		UNIT	NOTES	TEMP.(*K)	REFERENCES
Laser Properties		×	Å	t	700_			
Threshold Current	TCD	*********	-	(1)	(<u>A/cm²</u>)			
Density		20.0	7250		9x10 ²	vapor deposited.	78	Tietjen et al.
		40.5	6750		9x1.05	epitaxia, films	309	***************************************
		14	8105	26	9×10 ²	25% powe. output	300	
		10	7850		1.1-1.3x10 ³	Te-doped, vapor grown	77	Eligoev et al.
		15	7585			single crystal, apitaxia		221011 11 421
		20	7430			films 10-16; junction de		
		30	6892				- p - v.	
		35	6640					
		45	6390					
		30	6750			vapor grown, thin platelets	77	Johnson & Holonyak
Memory Effect, (Lifetime)			3 mill	isec.	at 6500 Å		77	Eliseev & Ismailov

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