Advances in light-emitting diodes

Short-range impurity states in ternary III–V compounds enhance radiative recombination rates, thereby aiding the color tunability of semiconductor lamps and lasers.

C. B. Duke and N. Holonyak Jr

The bright future of semiconductor lamps, especially "light-emitting diodes," is by now widely recognized. This recognition is fairly recent[1] even though the existence of light emission from semiconductor junctions has been known for almost twenty years. The transformation of LED's from laboratory devices to commercial products constitutes a good example of the effective interaction between solid-state materials technology and the quantum theory of condensed matter. Moreover, this interaction continues to generate changes in the materials, fabrication techniques and cost of LED's. In this article we will examine the influence of the fundamental principles of the quantum theory of solids on the design of semiconductor light emitters. Emphasis is placed on some of the more recently recognized consequences of these principles for tunable solid-state light sources. In particular, we describe how breakdowns of momentum conservation caused by the presence of neutral impurities in semiconductors has exerted a profound influence on the materials used to construct solid-state lamps.

The difficulty in the construction of semiconductor lamps arises because of three design criteria. First, the light emission must occur in the visible frequency range from the red ($\lambda \approx 6800$Å) to the blue ($\lambda \approx 4500$Å). Second, it must be possible to make a p–n junction (juxtaposed single-crystal positive- and negative-conducting regions) in the base semiconductor material. Third, the conversion of electrical energy to visible light at this junction must be relatively efficient. That is, the LED should have a luminous efficiency of 0.1–0.2 lumens/W or a brightness of 50–100 ft lamberts/ (A/cm^2) or higher. It is the difficulty of satisfying all three criteria simultaneously and inexpensively that has delayed the development of semiconductor lamps and visible semiconductor lasers.

Two recent developments have helped lessen this difficulty. The first is the occurrence of substantial advances in the chemistry of crystalline semiconductors, in particular the art of preparing ternary III–V semiconductor compounds, most notably $GaAs_{1-x}P_x$ and $In_{1-x}Ga_xP$. These materials crystallize in cubic lattices with one atom of a group III element such as gallium or indium associated with each atom of the group V element such as phosphorous or arsenic. The quantity x is the atomic fraction of one of the group III or V elements in a given alloy. The use of such ternary alloys is important for lamps because, by changing the value of the atomic fraction x, one changes the energy-band structure of the crystal and thereby alters the "color" of the light emitted from the junction. Thus, such alloys provide "tunable" solid-state light.

The second important new development is the recognition of the role of certain impurities in semiconductor light production. The most important of these is nitrogen, which was first studied in gallium-phosphide (GaP) by several groups at the Bell Telephone Laboratories.[3] Moreover, one of these groups undertook the initial study[4] of nitrogen in $GaAs_{1-x}P_x$. A more extensive examination of this system recently has been performed by George Craford and his coworkers at Monsanto[5] and by Holonyak and his coworkers at the University of Illinois.[6] The latter two groups also examined [7] the influence of nitrogen on light emission from $In_{1-x}Ga_xP$.

Called an "isoelectronic" trap because it has the same number of valence electrons as P or As, the nitrogen plays a significant role in rendering more efficient the light emission in these alloys at higher frequencies (orange to green in $GaAs_{1-x}P_x$, yellow to green in $In_{1-x}Ga_xP$ and green in GaP). Because in this article our concern is mainly the N-isoelectronic trap in ternary III–V compounds, the reader is referred to reference 1 for a detailed description of green-emitting N-doped and red-emitting Zn–O-doped GaP diodes.

Basic physical principles

Four central concepts underlie our understanding of light emission in semiconductors: The distinction between *direct* and *indirect* semiconductors, the role of conservation laws in determining the characteristics of radiative transitions in pure single-crystal semiconductors, the unique status of p–n junctions as the most efficient current-driven generators of non-equilibrium electron–hole pairs, and the breaking of the pure-crystal symmetry (and hence conservation laws) by impurity states. We describe the physical bases for semiconductor lamps by examining each of these concepts in turn.

Direct and indirect semiconductors. The first important physical concept is the distinction between *direct* and *indirect* semiconductors. This distinction is based on the nature of the energy-band structure of these materials. Electrons in pure semiconductors are characterized by a wave vector $\mathbf{k}$ defined to within a multiple of $2\pi/b$ where b is an appropriate crystal-lattice spacing. Formally, this wave vector is defined as the quantum number associated with the translational symmetry of the Schrödinger equation for the electron's wave function, ψ,

$$\left[\frac{-\hbar^2\nabla^2}{2m} + V(\mathbf{r}) - E(\mathbf{k})\right]\psi_{n\mathbf{k}}(\mathbf{r}) = 0 \quad (1)$$

in which $V(\mathbf{r})$ is the periodic crystal potential, attractive or repulsive in the

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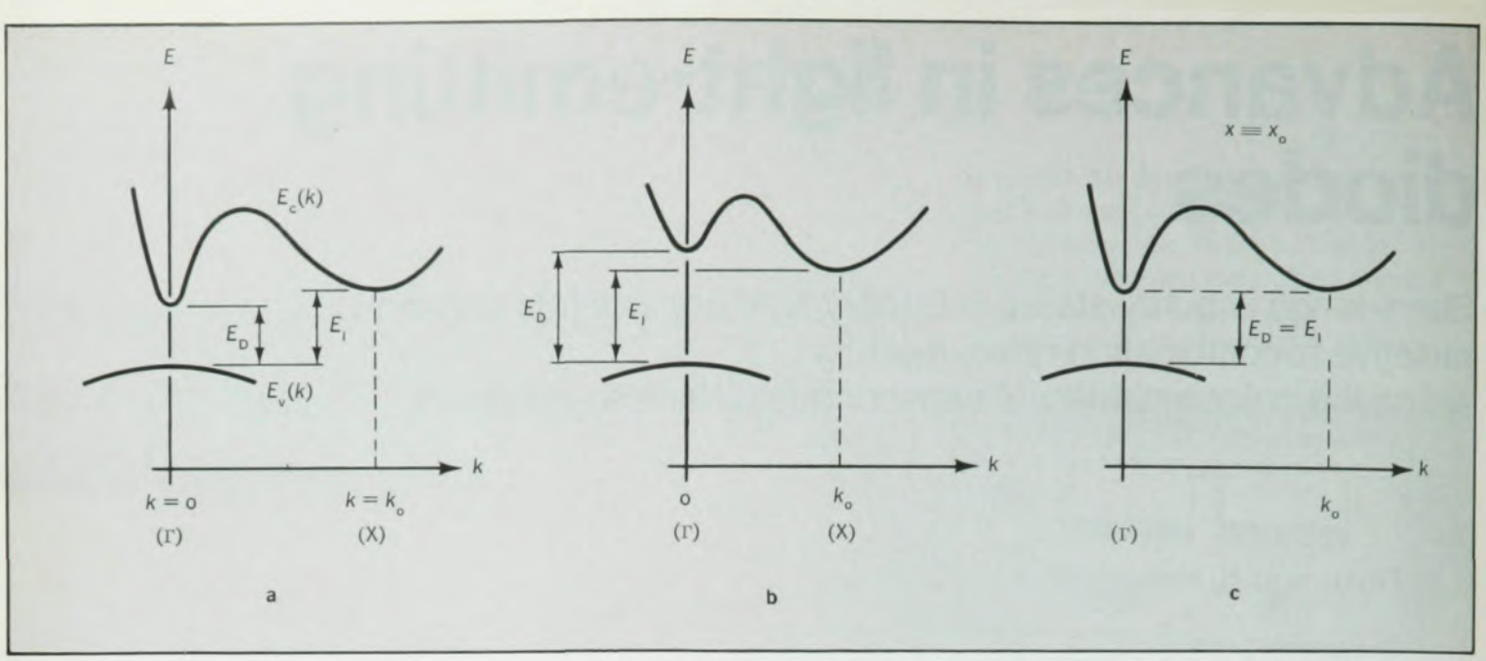


Energy bands of direct and indirect intrinsic (undoped) semiconductors are shown in curves a and b. As the composition variable, x, of ternary alloys such as $GaAs_{1-x}P_x$ and $In_{1-x}Ga_xP$ is changed, a crossover from "direct" to "indirect" type of semiconductor occurs when both minima in the conduction band are equal; this is shown in curve c. Figure 1

region of each of the atoms of the crystal. The invariance of $V(\mathbf{r})$ under translations that transform the crystal lattice into itself define the allowed values of $\mathbf{k}$.[8] Typical semiconductor one-electron energy bands are shown in figure 1. The lower-energy branch, designated by $E_v(\mathbf{k})$, specifies the energy of the semiconductor if an electron is removed from, and a "hole" is injected into, the semiconductor; these "valence-band" states are normally filled with electrons at low temperatures. The upper branch, designated by $E_c(\mathbf{k})$, specifies the energy of the system if an extra electron is injected into it; these "conduction-band" states normally are empty at low temperatures. As is evident from figure 1, a *direct* semiconductor is one in which the lowest-energy conduction-band state occurs at the same $\mathbf{k}$ value as the highest-energy valence-band state. An *indirect* semiconductor is one in which these maxima or minima occur at different values of $\mathbf{k}$, usually separated by $k_0 \approx 1\text{Å}^{-1}$. Some materials such as Si, Ge and GaP are indirect. Others such as GaAs and InP are direct. Therefore, in alloys such as $GaAs_{1-x}P_x$ (GaAs + GaP) and $In_{1-x}Ga_xP$ (InP + GaP), a transition between *direct* and *indirect* occurs at some critical value $x = x_c$. The energy-band structure at this composition is indicated in figure 1c.

Conservation of energy and wave vector. When light is absorbed by a semiconductor, an electron of momentum $\mathbf{k}_h$ from the valence band is excited to the conduction band into a state, $\mathbf{k}_e$, by the absorption of a quantum of electromagnetic energy, of energy E, $E = h\nu = \hbar ck$. The conservation of momentum and energy in this absorption process requires

$$\mathbf{k}_e - \mathbf{k}_h = \mathbf{k} \qquad (2a)$$

and

$$E_c(\mathbf{k}_e) - E_v(\mathbf{k}_h) = h\nu \qquad (2b)$$

We know, however, that for a semiconductor the energy gap ($E_c - E_v$) is about 1 eV; so that for a photon of this energy $k = (1\text{ eV})/c\hbar \approx 10^{-3}\text{ Å}^{-1}$. As both k_e and k_h are of the order of 10^{-1} Å^{-1}, we see that $k \ll k_e, k_h$. Therefore, we speak of the photon as causing a *vertical transition* for which $\mathbf{k}_e = \mathbf{k}_h$, as shown in figure 2a. That is, the photon can neither contribute nor carry away much momentum. Comparison of figure 2a with figure 1 reveals that such *vertical* (no $\mathbf{k}$-change) transitions cause light absorption at the energy of the smallest energy gap in the semiconductor only for direct semiconductors. For indirect semiconductors, these transitions cause absorption only above the energy of the direct gap ($h\nu > E_D$). Absorption for energies above that of the indirect gap but below that of the direct gap ($E_D > h\nu > E_I$) occurs only via a *diagonal transition* as illustrated in figure 2b. To conserve momentum, the excitation of the electron must be accompanied ("assisted") by the scattering of the electron from a lattice vibration ("phonon") or impurity potential. Therefore, these diagonal transitions usually are much less likely than vertical ones that do not require any assistance.

Need for p–n junctions. The quantum emission of light by semiconductors occurs via the inverse of the photon absorption processes shown in figure 2. An electron in the upper conduction band makes a transition to an empty state in the lower valence band and recombines with a "hole" radiating light in order to conserve energy. Unlike the absorption of light by a semiconductor, however, light emission does not occur in a material in thermal equilibrium near room temperature because the electronic states in the conduction band are mainly empty and those in the valence band are mainly full. Consequently, any complete discussion of the emission process requires consideration of the mechanism for generating simultaneously non-equilibrium populations of excited "electrons" in the conduction band and "holes" in the valence band.

An important point now arises because under most circumstances excited electrons are injected into the lowest-energy conduction-band states, and excited holes occur in the highest-energy valence-band states. Therefore, in an indirect semiconductor, the excited electrons and holes exhibit widely different values of momentum. Because of this, they must undergo indirect transitions to emit light, and consequently, such light-emitting processes are relatively rare.

We may now consider one of the major difficulties in making efficient visible solid-state lamps. The III-V direct semiconductors (see figure 1a) have band gaps in the infrared ($E_D \leq 1.7$ eV). These direct compounds are made with heavy atoms, such as In, As and Sb. To get band gaps in the visible region ($1.8 \leq E_g \leq 2.9$ eV), one must use lighter elements such as Ga, Al and P. Compounds made with these materials are indirect (see figure 1b). Consequently, in pure form, they exhibit only weak diagonal light-ab-

sorbing or light-emitting transitions (figure 2b). They thus make poor lamps and do not exhibit laser operation at all.

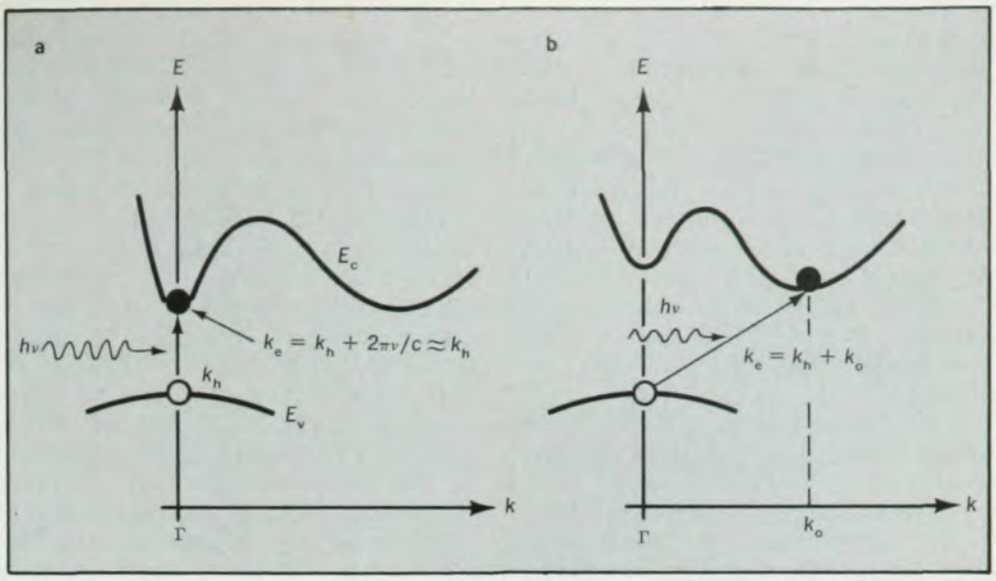
When confronted with this problem in the early 1960's, many workers posed the question, "Can direct semiconductors be found with band gaps in the range $1.8 \leq E_D \leq 2.9$ eV?" The answer is "Yes." Many II–VI compounds, such as CdS, exhibit direct band gaps in the visible region of the energy spectrum. Thus began what has been, to date, one of the fruitless episodes in the story of semiconductor lamps.[9] In order to make a lamp one needs not only an efficient recombination process, but, as we stressed earlier, also a current-driven method of generating nonequilibrium populations of electrons and holes that will recombine in the same region of the crystal. The only efficient means of accomplishing this is via a p–n junction. A unique feature of the III–V alloy semiconductors is that p–n junctions can be made from them. In spite of the many man-years devoted to the effort, such junctions have not yet been made in the II–VI materials that exhibit direct band gaps at energies corresponding to the visible spectrum. Indeed, a decade or more of effort at several industrial laboratories has been invested in the so far unsuccessful effort to make efficient junction lamps out of this class of direct semiconductor materials. In retrospect, this fact seems particularly ironic when we recall that at the time the first semiconductor lasers were built (1962), the III–V crystal $GaAs_{1-x}P_x$ was synthesized and made into a laser junction in the red portion of the spectrum,[2] thereby indicating that III–V alloys clearly were one of the "right" choices of materials in which to make visible semiconductor lamps.

We have now established three key facts:

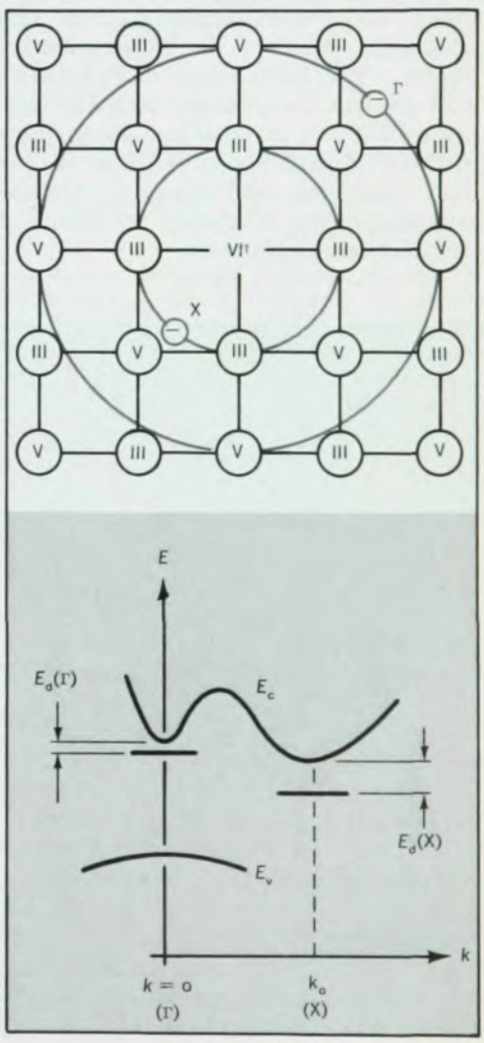
- The *direct* band gaps in *binary* III–V semiconductors have energies corresponding to infrared rather than visible frequencies (excluding GaN).
- Classes of other materials exhibiting direct band gaps at energies associated with visible light do not admit the construction of p–n junctions, which are required if both electrons and holes are to be injected efficiently.
- Because of the first two facts, we are constrained to consider the III–V ternary and quaternary alloys. The group IV semiconductors (C, Si, Ge) and their alloys are inappropriate because all of them are indirect semiconductors.

Role of impurities. Two further questions arise at this point. Can III–V ternary alloys be grown in the quantity, size and quality required for inexpensive mass production? What range of colors is available from only *direct* alloys? Considerable progress has been made since 1960 (when the first junction was made in $GaAs_{1-x}P_x$) in fabricating junction lamps and lasers in ternary III–V alloys. The $GaAs_{1-x}P_x$ alloys[10] currently form the host for a product line of red lamps. The recent availability of fairly high-quality direct-bandgap $In_{1-x}Ga_xP$ has led to the construction of experimental junction lasers[11] in the red, and lamps from the infrared to the yellow[1,11]. To obtain lamps in the yellow-green and green portions of the spectrum, however, it is always necessary to use indirect semiconductors even in III–V ternary and quaternary alloys. Therefore we turn to the fourth and final central concept of light emission in semiconductors: the role of impurities in breaking the symmetry (and hence momentum conservation laws) characteristic of pure materials.

For its symmetry-breaking role, an impurity's most important property is the range of the force it exerts on an electron. Charged impurities such as zinc and tellurium exhibit long-range forces, and neutral impurities such as nitrogen and bismuth exhibit short-range ones. For example, a group II impurity (acceptor) is incorporated into a III–V semiconductor lattice as essentially a "point" negative charge. Under the influence of the electrostatic potential of the negatively charged group II acceptor, a hole becomes bound to the acceptor. Similarly, a group VI element is incorporated into a III–V alloy as a positively charged "donor" impurity. The resulting electron orbits and energy-level diagram are shown in figure 3. Because of the long range of the Coulomb potential, each minimum in the conduction band



Radiative transitions. Part a shows a vertical transition ($\mathbf{k}_e = \mathbf{k}_h$) in a direct semiconductor, induced by the absorption of light. Part b shows a diagonal transition ($\mathbf{k}_e = \mathbf{k}_h + \mathbf{k}_0$) in an indirect semiconductor induced by the absorption of light together with the emission or absorption of a lattice vibration. An excited electron can make a radiative transition to an empty valence-band state by the inverse of these light-absorption processes. Figure 2



Electron orbits and bound states associated with a charged column-VI donor impurity in a III–V compound. The orbit associated with the lowest trap state composed of conduction-band eigenstates near $k = 0$ is labeled by Γ. The orbit associated with states near the zone boundary k_0 is labeled by X. Figure 3

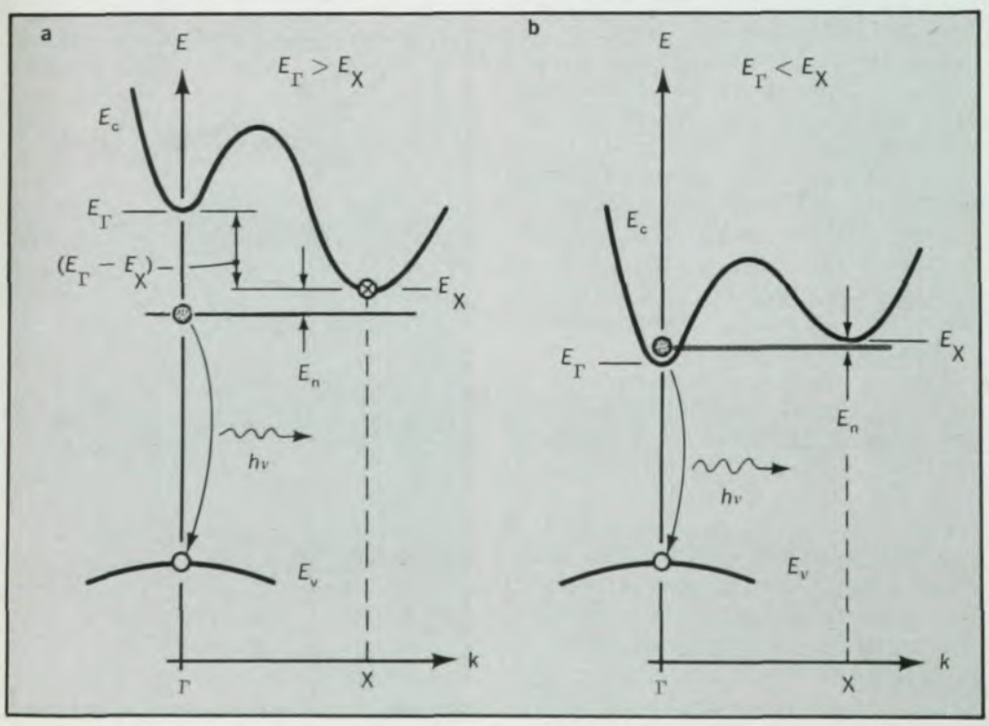
or maximum in the valence band is associated with a separate and distinct spectrum of spatially localized ground and excited states. That is, in the case of two minima in the conduction band the long range of the donor potential causes states from a relatively small volume of the Brillouin zone to be mixed together to give two donor "ground" states of the electron with binding energies designated by $E_d(\Gamma)$ and $E_d(X)$, respectively, in figure 3.[12] The importance of this result is that the Coulomb potential associated with either acceptors or donors is relatively ineffective in breaking the pure-crystal momentum conservation law.

For our purposes, the most important feature of the nitrogen isoelectronic trap is the short range (several atomic distances) of its electronic potential. The attractive nature of this potential leads to the binding of an electron with energy $E_N \approx 10$ meV. Its short range, however, leads to the existence of only a single electronic bound state composed of conduction-band states from throughout the first Brillouin zone[4,6,7,13] in momentum space. The short range of this potential renders the nitrogen uniquely suited for its role in breaking the momentum-conservation selection rule in optical absorption and emission, thereby enhancing the efficiency of lamps in indirect semiconductors.

The short-range of the nitrogen potential causes another, perhaps more surprising, effect. While strong enough to bind an electron from conduction-band states near X ($k \approx k_0$ in figure 1), it is too weak to create a bound state from those near Γ ($k \approx 0$, in figure 1). Therefore, as the crystal composition variable, x, in the ternary alloy is altered to render the semiconductor direct, the energy of the nitrogen bound state remains about 10–50 meV below the conduction-band minima at the X point [$\mathbf{k} \approx (\pi/b, 0, 0)$, see figure 4a]. When by virtue of varying x, the direct minimum at Γ passes below the electron binding energy of the N-trap, the electron remains "almost" trapped in a resonant state above this minimum as indicated in figure 4b. This resonance is associated with two important optical phenomena in ternary III–V alloys: The occurrence of line emission at energies *above* that of the band gap in direct semiconductors, and the resonant enhancement of the intensity of the emission from the N-state when its bound (or "resonance") state energy is approximately equal to that of the conduction band minimum at Γ.[14]

A final significant feature of the N-trap potential is its electrical neutrality. If an electron is bound to it, the system of N-plus-electron is a negatively charged center. This center binds a hole from the valence band, leading to a neutral N-plus-electron-plus-hole complex called a "bound exciton." Its localization of *both* the electron and the hole in the same region of the solid renders the nitrogen even more effective in breaking the pure-crystal momentum conservation law. Indeed, other isoelectronic traps with more tightly bound electron–hole pairs (for example, Zn–O pairs in GaP) are associated with a still higher efficiency generation of light. Such systems are interesting because increased localization of the electron–hole wave function is associated with a reduced energy of the radiative transition. Thus, light of several colors can be generated using a wide-band-gap III–V compound as the host and different impurities to generate the individual colors. For example, yellow and green light can be generated by doping GaP with nitrogen, and red light can be generated by doping it with zinc and oxygen.[3]

Summarizing, we can say that to obtain direct semiconductors appropriate for efficient light generation at frequencies above that of red it is necessary to use ternary III–V alloys. Even in these alloys, the maximum direct band gap in $In_{0.7}Ga_{0.3}P$ corresponds to light emission in the yellow. Hence, impurity-assisted light emission is required in the blue-green in all cases, and in the red through green in binary III–V alloys.

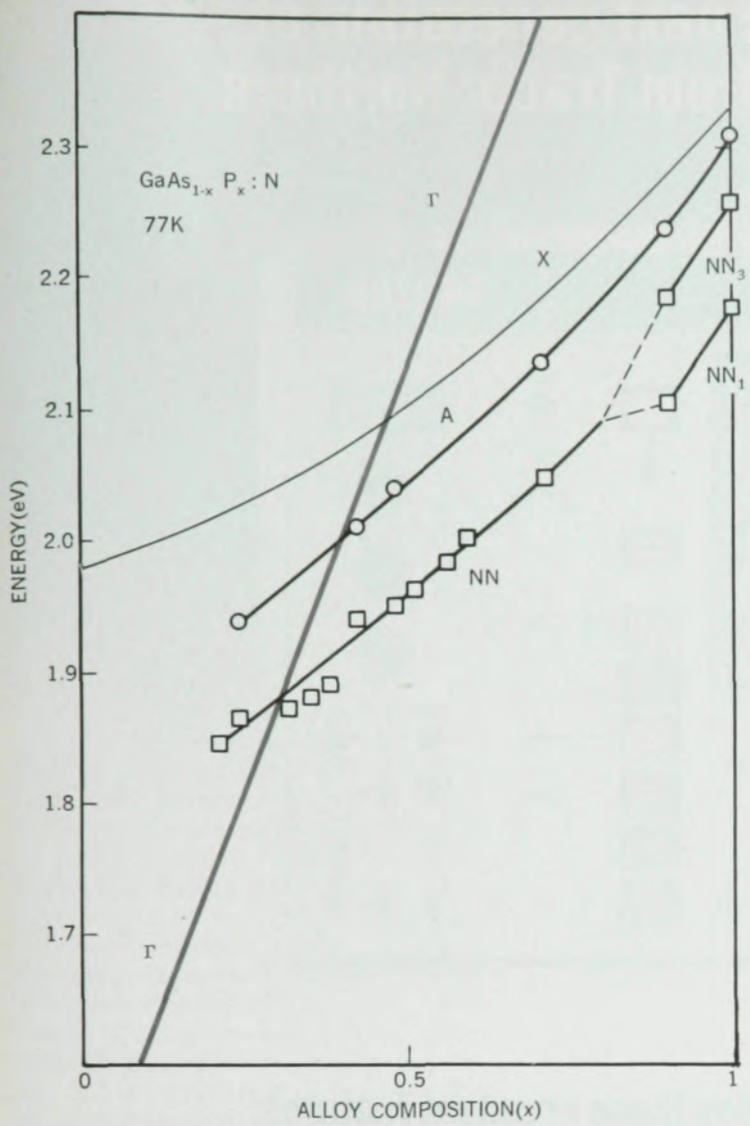


Radiative recombination from a nitrogen isoelectronic trap state *below* (curve a) the conduction-band edges at both Γ and X in a III–V alloy semiconductor. The electron is captured into this state from conduction-band states near X. However, it radiatively combines with the hole via Fourier components of its wave function near Γ. The intensity of this recombination increases as $E_\Gamma - E_X$ decreases. Radiative recombination from a nitrogen isoelectronic resonant trap state *above* (curve b) the conduction-band edge ($E_X - E_N - E_\Gamma$) in a direct III–V alloy semiconductor. The length of the gray line associated with the trap state indicates that the state is built from continuum states from throughout the conduction band. The width of the gray line indicates that the electron is in a resonant state of finite width that can be scattered into a continuum conduction-band state near $k = 0$. Figure 4

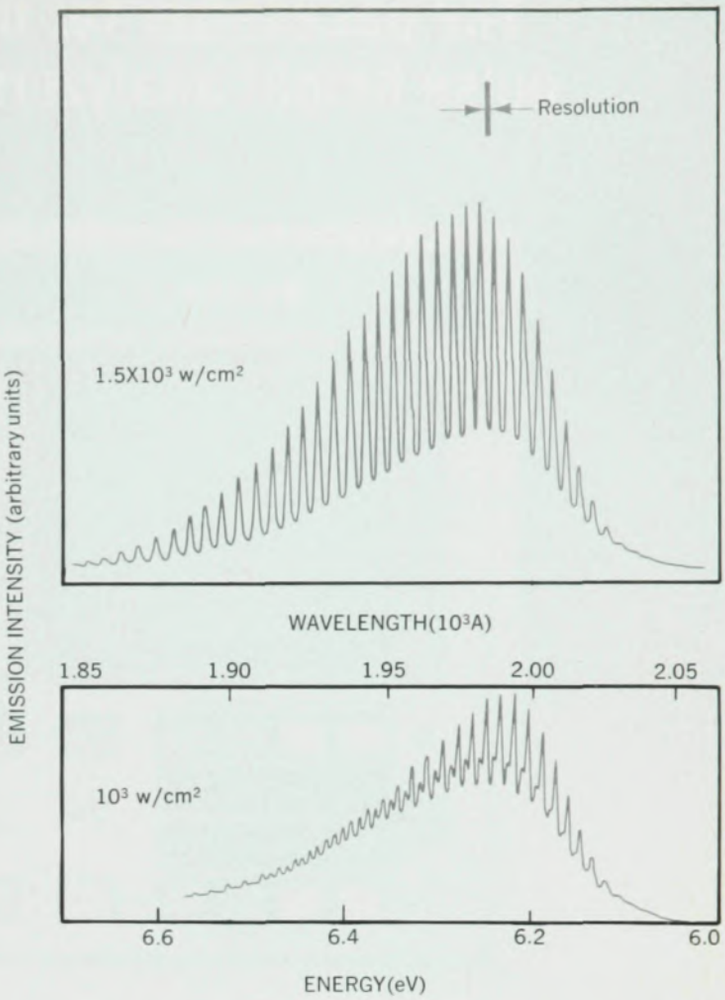
N-doped alloy semiconductors

Two approaches have gained acceptance for the construction of LED's. The first, advocated primarily by workers at the Bell Telephone Laboratories,[3] consists of selecting a wide-band-gap indirect binary semiconductor host, namely GaP, and utilizing different dopants to generate various colors via impurity-assisted light emission. The major advantage of this approach is the presumed ease of growing crystals of the host material. Its main disadvantage is lack of simultaneous control over the color and efficiency of the resulting lamps. The second approach, advocated by workers at Monsanto,[5,10] consists of utilizing *direct* III–V ternary alloys where possible,[2] and nitrogen-doped alloys otherwise. Although in this approach the host materials might appear more difficult to grow,[10,14] the method permits the vapor-epitaxial growth of large crystals, the simultaneous control over the color and efficiency of the lamps and the construction of lasers in addition to lamps. Since the characteristics of the GaP system have been discussed extensively elsewhere,[1] we turn here to a discussion of the properties of III–V ternary alloys.

Lamps versus lasers. First, we dis-



Photon emission energy versus alloy composition x, for an electron–hole recombination transition (A line) involving individual N traps in $GaAs_{1-x}P_x$. Also shown are NN pair transition lines. Γ and X show how the direct and indirect band edges vary with alloy composition. Notice the direct–indirect (Γ − X) crossover at $x = x_c = 0.46$. Figure 5



Stimulated emission spectra of N–N pair isoelectronic-trap recombination transitions in $GaAs_{1-x}P_x$ ($x = 0.56 > x_c$) excited with an argon laser. The cavity-mode spacing is set by the sample geometry, which is that of a highly perfect whisker of flattened-hexagonal cross section imbedded into an indium heat sink. At an excitation level of $10^3 W/cm^2$, two sets of sample modes (one parasitic) are excited. At the higher pumping level of 1.5×10^3 W/cm² one set of modes dominates and deepens, and the emission line broadens—characteristic of an "inhomogeneously broadened" laser. Figure 6

tinguish between spontaneous radiative recombination and "stimulated" emission, which is the enhancement of the recombination process caused by the high electric field arising from emitted photons that are partially "trapped" by the boundaries of the crystal. If the electron–hole recombination in a p–n junction is spontaneous, we have an LED. If the injection level is higher and the recombination becomes stimulated in a diode (or photopumped wafer) shaped to have good reflecting side walls (a Fabry–Perot resonator), we have a laser. Until recently semiconductor lasers operated only on direct interband transitions; the type of transition characterized by figure 2a. This has changed, however, with the introduction of nitrogen into $GaAs_{1-x}P_x$ and $In_{1-x}Ga_xP$. Transitions associated with N-trap states in these ternary alloys are strong enough to support stimulated emission provided ($E_\Gamma - E_X$) is sufficiently small. Thus, one obtains the important new result that lasers as well as lamps can be made from indirect semiconductors.[16]

Resonant impurity recombination. We recall that one of the consequences of a short-range trap potential in a ternary III-V alloy is an enhancement of the radiative-recombination probability when its electron bound-state energy ($E_X - E_N$) occurs near that of the conduction band minimum at Γ (see figure 4b). An experimental realization of this idea was provided by the observation that in the alloy $GaAs_{0.65}P_{0.35}$:N, states associated with the N-trap exhibit stimulated emission.[6] As may be seen from figure 5, in which the energies of the various band minima (figure 1) and N-trap states (figures 4a and 4b) are plotted as a function of crystal composition, the crystal is direct, and the N-trap state is a *bona fide* bound state ($E_\Gamma > (E_X - E_N)$). Although the crystal is direct, this observation of stimulated emission nevertheless illustrates an important result: N-trap transitions can exhibit a strength comparable to that of direct, interband transitions.

What are the consequences of varying the crystal composition? As we decrease x below x_c, $E_X - E_\Gamma$ increases. The N-trap, however, is dominated by and "attached" to E_X. Thus we might expect the behavior indicated in figure 4b: If $x \ll x_c$ the N-trap state is thrust up into the conduction band at Γ as a resonance. In such a case, a photoluminescence line could be excited at energies above that of the fundamental smallest energy gap of the crystal. This phenomenon has been seen by the Illinois group[6] in $GaAs_{1-x}P_x$, subsequently by them[7] in $In_{1-x}Ga_xP$ and also by Soviet scientists at the Lebedev Institute, working with silicon doped with oxygen.[17] Indeed, these photoluminescence processes are so strong that they exhibit laser operation.[14]

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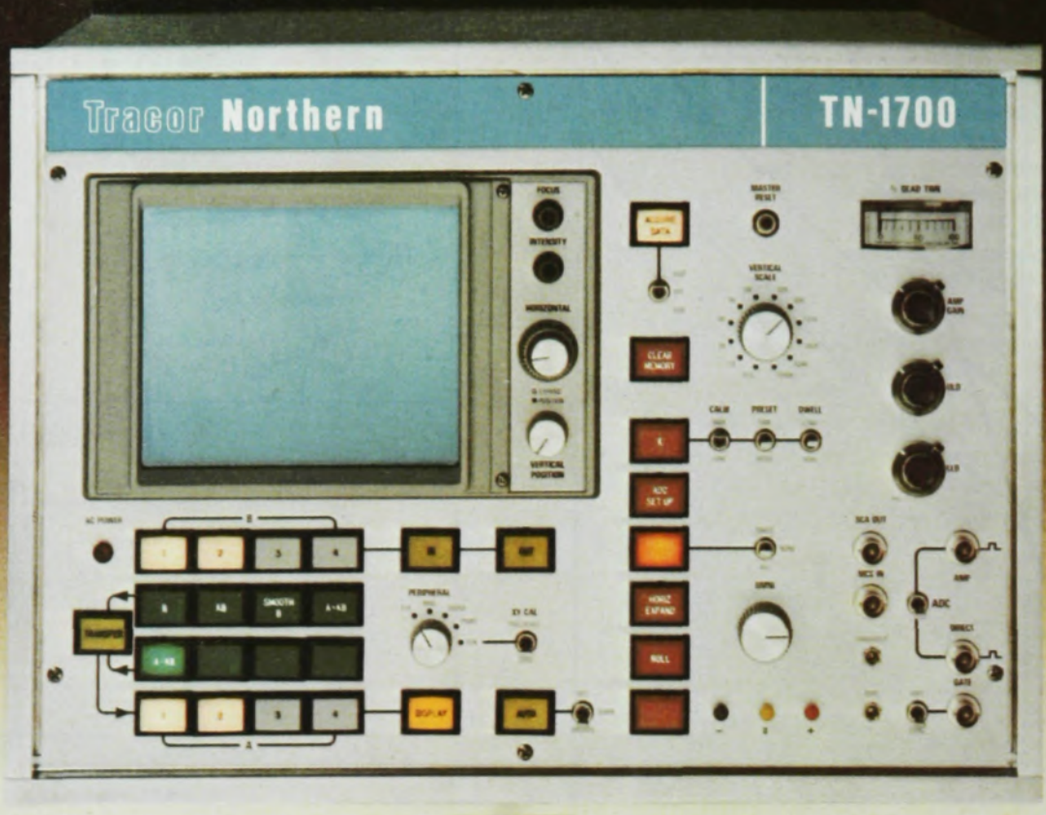

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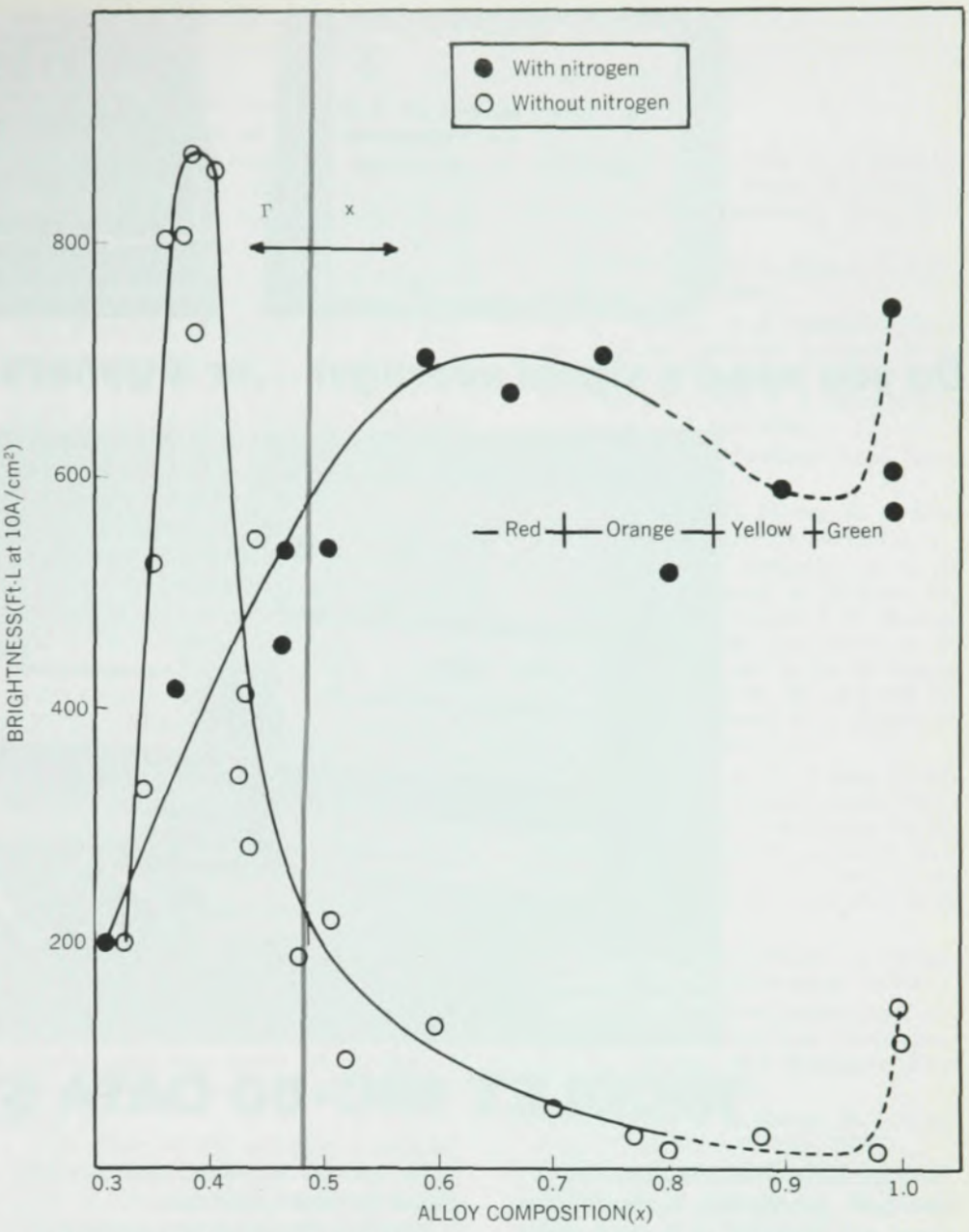
We now come to one of the most significant issues of all: What happens to the N-trap recombination transitions when the host ternary alloy becomes indirect? In this situation $E_\Gamma > E_X$, but the recombination involving the nitrogen does not change abruptly even though the crystal is now indirect. Consequently, stimulated emission can be observed[16] in samples of indirect $GaAs_{1-x}P_x$ and $In_{1-x}Ga_xP$. Before discussing these observations, however, it is necessary to introduce one final concept: the idea of an electron–hole transition involving more than one nitrogen atom.

If an extra electron (and hole) is injected into the crystal and the nitrogen atoms are numerous (10^{18}–10^{20}/cm^3), then the electron often is not bound to an isolated N potential. Rather, nearby nitrogen atoms establish a stronger "pair" potential. These "N–N pairs," which exist in numerous directions and at varying spacings in the crystal, can bind the electron in a co-operative potential. They lead to larger electronic binding energies (approximately 100 meV), and hence lower photon emission energies than in the case of a single nitrogen atom ($E_N \approx 10$ meV). Workers at the Bell Telephone Laboratories have shown[3] that in GaP both individual nitrogen atoms and N–N pairs trap electrons. At low temperatures each electron subsequently binds a hole, leading to well-defined *sharp* recombination lines. This is not the case in the ternaries $GaAs_{1-x}P_x$ and $In_{1-x}Ga_xP$ because of the random distribution of As–P or In–Ga in these alloys. Neither individual nitrogen atoms nor the various N–N pairs experience exactly the same As–P or In–Ga environment. This limitation leads to the smearing of the recombination radiation into a broad spectrum, over 100 meV wide. In fact, the N-emission line indicated in figure 5 may have been broadened and shifted to lower energies by as much as 100 meV relative to its energy in GaP, particularly when N–N pair emission is dominant—for example, at high nitrogen doping levels.

We consider finally the experimental situation for an N-doped indirect $GaAs_{1-x}P_x$ crystal. A crystal with $x = 0.56$ is clearly indirect because x_c, defined in figure 1c, is approximately equal to 0.46 in $GaAs_{1-x}P_x$ (see figure 5). In this case, E_Γ(labeled "Γ" in figure 4a) is greater than E_X (labeled "X" in figure 5) by over 100 meV. We have noted, however, that this fact does not weaken excessively the ability of the N (or N–N pair) trap to promote efficient electron–hole recombination. A convenient sample configuration for photoexcitation is provided by perfect crystal whiskers, shaped naturally in the form of prisms and sometimes only about 10 microns in "diameter."

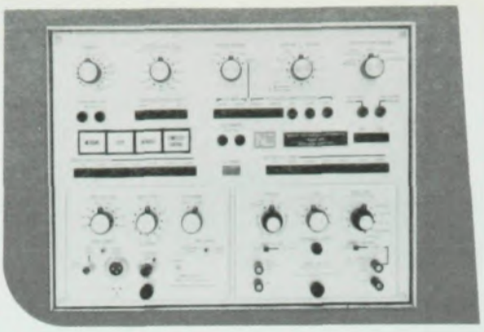


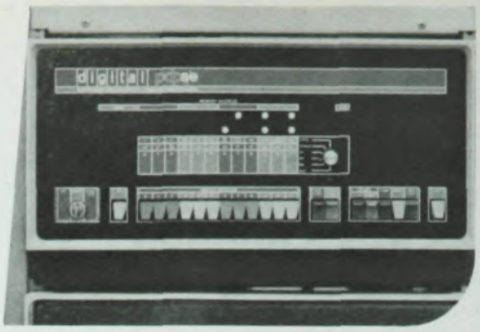
The brightness of $GaAs_{1-x}P_x$ LED's in the red-orange-yellow-green spectral range for p–n junctions with nitrogen doping (solid data points) and without nitrogen doping (open circles). Notice that the brightness of the diodes without N (open circles) begins to drop before the direct–indirect transition ($\Gamma \leftarrow X$) because of the premature intrusion of "indirect" crystal behavior. The large increases in brightness due to N doping become somewhat larger as the $GaAs_{1-x}P_x$ alloy approaches GaP ($x \rightarrow 1$) and alloy disorder (As–P disorder) fades, for example, the point at $x = 1$ for GaP:N. This figure is taken from reference 18 by Craford and his collaborators.

Figure 7

These whiskers have regular, flat reflecting faces that form high-quality optical resonators. The behavior of such a $GaAs_{1-x}P_x$ ($x = 0.56$) whisker imbedded into an indium heat sink and then pumped (photoexcited) with an argon laser is shown in figure 6. The large width of the emission line is due to electron–hole recombination on N–N trap centers. At the lower pumping level a main set of resonator modes is seen as well as a parasitic set that diminishes in competition with the other set at a higher pumping level. This behavior is indicative of stimulated emission, as are the large changes in resonator mode amplitude and width of the emission with a small change in pumping intensity.[16]

An interesting feature of the stimulated emission exhibited by the particular *indirect* sample whose spectrum is shown in figure 6 is that it is more characteristic of the behavior of a gas laser than that of previously studied semiconductor lasers. As electrons recombine on N–N pair centers in a given region of the spectrum, the electrons on other N–N pair traps (neighboring in energy) cannot readjust fast enough to provide a continual source of electrons. This fact leads to the type of broadened spectral characteristic seen in figure 6, which is referred to as an inhomogeneously broadened emission "line." Such broadened emission is characteristic of optically pumped lasers in insulating materials such as the famous ruby laser; so we see that the N–N pairs in III–V alloys form a





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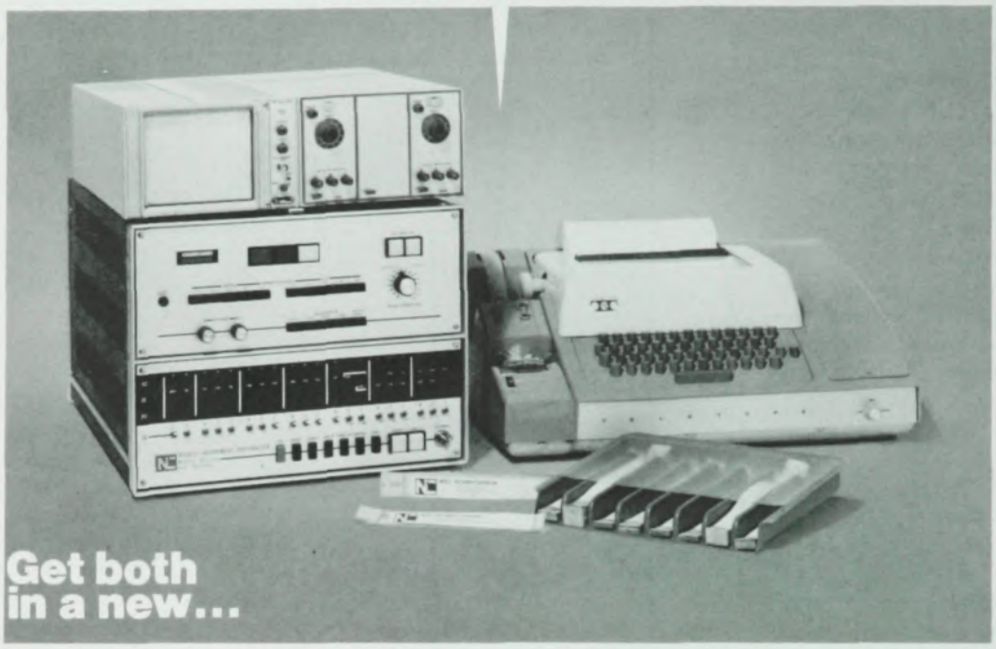

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bridge between conventional direct-gap semiconductor lasers in which the line narrows with increasing pump power and the familiar impurity-induced laser action in insulators. For indirect $In_{1-x}Ga_xP$, however, stimulated emission has also been observed on the nitrogen A-line transition,[7] which exhibits its spectral narrowing like the more familiar examples of laser operation on interband transitions in direct semiconductors.

Practical considerations

At the present state of the art, the growth of $In_{1-x}Ga_xP$, although promising and beginning to receive considerable attention, is not as highly developed as is that of $GaAs_{1-x}P_x$ (or GaP). $GaAs_{1-x}P_x$ is grown by commercial gaseous processes on large GaAs substrates. Then p–n junctions in the form of LED's, or arrays of letter symbols and numerals, are prepared by well-developed integrated circuitry techniques, such as by conventional oxide deposition, photolithographic and chemical shaping of characters, and finally impurity diffusion to form the p–n junction symbols and characters. No processing technology in electronics is more highly developed or economical; this is a tremendous production advantage for the $GaAs_{1-x}P_x$ light-emitting device. In addition the wavelength is tunable by varying the crystal-composition variable x, and the N-trap makes even indirect $GaAs_{1-x}P_x$ crystals efficient in the conversion of current to light. The result is a burgeoning LED industry producing light-emitting devices that can be used in countless read-out and display applications: small calculators (such as the HP-35), automobile instrument panels, electronic instruments, watches and clocks, indicators (ON, OFF, temperature, etc.) in household and industrial appliances and equipment, fault indicators in electronic circuitry, warning symbols, pilot "lamps" in transistorized equipment, display symbols in computer data terminals, and numerous others.

Prior to 1971 all $GaAs_{1-x}P_x$ LED's were designed so that the crystal energy gap (E_Γ) was as high as possible, but *direct* ($x = 0.40 - 0.46 \leq x_c$; see figure 4a), in order to give a strong, high-efficiency electron–hole recombination transition. The energy gap was chosen to put the energy of the emitted photon as far from the dull red and into the brighter red (toward the orange) as possible. The eye's sensitivity improves dramatically from the red into the orange, peaks at the yellow and yellow-green, and then declines from the green into the blue. Unfortunately, the $E_\Gamma - E_X$ crossover (x_c, figures 1 and 5) occurs at a composition with too small an energy gap to permit direct interband recombination at the colors characteristic of the highest eye sensitivity.

Within the last two years Craford and his coworkers at Monsanto[5] have introduced the nitrogen trap into $GaAs_{1-x}P_x$ LED's. For green emission it also can be inserted into the ternary endpoint, the binary GaP. With the assistance of the N-trap, the strength of the radiative-recombination transition is enhanced throughout the indirect composition range of $GaAs_{1-x}P_x$ ($0.49 \leq x \leq 1$, 300 K). Thus, we can build a strong light emitter of tunable wavelength from red to green utilizing the nitrogen-assisted recombination processes. The practical effect is indicated in figure 7, which shows the brightness of $GaAs_{1-x}P_x$ LED's fabricated in the Monsanto Laboratories as a function of crystal composition with and without nitrogen in the crystal. In more recent work Craford and coworkers[18] constructed orange $GaAs_{1-x}P_x$:N LED's yielding 0.4 lumens/watt. This performance can be rivaled only by Zn-O-doped red GaP diodes[1] of external quantum efficiency exceeding 2%. Although 10%-efficient Zn-O-doped GaP diodes have been built in the laboratory, commercial units exhibit an external quantum efficiency of typically 1–2%, and are not as easily mass produced as $GaAs_{1-x}P_x$:N LED's. In addition, $GaAs_{1-x}P_x$:N LED's have a steeper, more conductive I–V characteristic, and can easily be strobed or pulse operated, as in the HP-35 calculator.

The effect of the nitrogen is evident. When inserted into a ternary III–V alloy, it has provided for the first time a *continuous range* of colors, from red through green, over which bright LED's are possible. Furthermore, nitrogen is just beginning to be used in commercial $GaAs_{1-x}P_x$ LED's and the processing of $InGa_{1-x}P_x$ is undergoing further refinement that may yet lead to the commercial utilization of these alloys in LED's or semiconductor lasers. Thus we see that the combination of short-range traps and recent improvements in the materials technology of ternary III–V alloys are adding a further dimension to the physical possibilities in the design of tunable, efficient and inexpensive semiconductor light sources.

* * *

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