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Visible Light from Semiconductors

Luminescence from *p-n* junctions and potential uses of solid state light sources are discussed.

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With the advent of the electronic age, there has been a need for sources of visible light in the form of fast, tiny, reliable devices compatible with present electronic circuitry. Often, miniature versions of conventional lamps such as tungsten bulbs are used for these purposes. Although these work satisfactorily in most respects, they have some undesirable properties. For example, they have a short lifetime, a slow switching speed, and a proneness to sudden or catastrophic failures. In this article, the basic characteristics of semiconductor diodes that emit visible light are discussed.

In general, light is generated by one of two mechanisms, incandescence and luminescence. Incandescence is the radiation emitted by matter as a consequence of the thermal motion of its constituent atoms. Spectroscopically, the radiation due to this thermal motion has a broad-band distribution. Most of the emitted radiation occurs in the infrared region of the spectrum. Of the total input energy in a typical household lamp with a 500-hour lifetime, about 7 percent is converted into visible radiation.

Luminescence is light emission in a narrow band, and hence the light is more monochromatic. This emission results from a transition of electrons from a higher energy state to a lower energy state. The luminescent source is at the ambient temperature, and the emission of radiation does not change the temperature significantly. Examples of light sources dependent on the luminescence mechanism are fluorescent lights and gas-discharge lamps. In both cases, the photon emission arises from electronic transitions occurring in atoms in the gas phase. In the former, the initial photon is absorbed in a phosphor and reemitted by it at lower energy, that is, energy in the visible range of the spectrum. In gas-discharge lamps, the photon emitted by the gaseous atoms is used directly. Lamps made of semiconductor crystals also belong to this group, and the light generated from them is called electroluminescence. Spectra of a typical incandescent bulb and of a gallium phosphide electroluminescent light source are shown in Fig. 1, together with the sensitivity curve of the eye.

Let us now consider the origin of luminescence and of the relevant electronic energy states, first of isolated atoms and then of solids. The occupied ground state (V) of an atom is shown in Fig. 2a, along with some excited states. If the correct amount of energy, δE, is absorbed by the atom, then the electron makes a transition to the first excited state (C). Similarly, the electron can be raised to higher-lying excited states. The reverse process is shown in Fig. 2b. Here the electron returns to its ground state with the emission of a quantum of energy δE. The emitted energy is shown as a photon of energy $h\nu$, where h is Planck's constant and ν is the frequency of the light.

In the case of solids, the atoms no longer act as independent entities. Instead of the sharp, single-valued electronic states of the isolated atom, the electronic states of the atoms in the solid merge into bands where the states are no longer identifiable with the individual atoms. The pertinent energy bands of a semiconductor are shown schematically in Fig. 2c. The lower valence band (*V.B.*) is the highest-lying band filled with electrons; and *C.B.* is the normally unoccupied conduction band. The two bands are separated by a forbidden energy zone of width E_G. This is the energy gap, and in the ideal crystal there are no allowed states in this gap, hence the term forbidden zone. If the valence band is completely filled and the conduction band is completely empty, then the solid behaves as an insulator, that is, the application of an external electric field is unable to produce a displacement of charge. This is the case for an ideal, perfect semiconductor crystal at the absolute zero of temperature. Fortunately, actual crystals are imperfect, and the imperfections are the reason for most of the interesting properties of semiconductors.

There are different types of imperfections, but we will consider only two types commonly known as donors and acceptors. If on a site in the crystal lattice normally occupied by an atom of the host crystal, another kind of atom (an impurity atom) is present, the resulting imperfection is called an atomic point defect. The nature of the defect depends on the electronic structure of the substituting atom in comparison to that of the displaced atom of the host crystal. If the defect-producing atom has one more outer, or planetary, electron than the original resident at the site, it will be a donor; thus, in the simplest case, it will introduce an electron in the forbidden gap below the conduction band and separated from it by an energy:

$$E_D = \frac{13.6}{\varepsilon} \cdot \frac{m^*}{m_0} \text{ (electron volt)}$$

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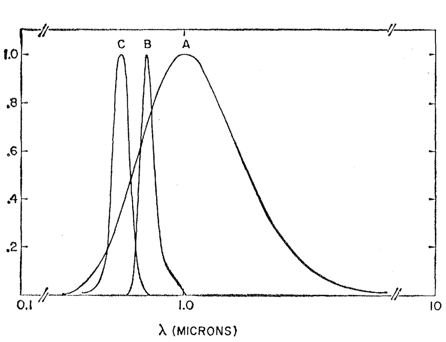


Fig. 1. Curves. (*A*) Spectrum of a typical incandescent lamp with a filament temperature of 2600°C. (*B*) Spectral curve of a red-emitting gallium phosphide diode. (*C*) Visibility curve for the human eye.

Here E_D is the binding energy of the donor. This expression represents the ionization energy of a hydrogen atom as modified by ε, the dielectric constant of the host crystal, and by the ratio of the effective to the free-electron mass, m^*/m_0. A diagram of the energy relations in a crystal containing donors is shown in Fig. 3a. Typical binding energies are of the order of 0.01 to 0.1 electron volt. Consequently, the electrons can be thermally excited into the conduction band where they can carry current if an electromotive force is applied.

Impurity atoms that have one less planetary or outer electron are known as acceptors. They introduce unfilled electronic states above the valence band and separated from it by an energy E_A. If E_A is of the order of 0.01 to 0.1 electron volt, then electrons from the valence band can be thermally excited into the acceptor levels. The resulting unoccupied valence band states are called holes. If an electric force is applied, current will flow in the valence band by displacing the holes opposite to the flow of electrons. Hence, the holes may be considered to be positively charged particles. The resulting charge transport is referred to as hole or *p*-type conductivity (Fig. 3b).

Another factor that is important in a discussion of semiconductors is the "Fermi level." It describes the distribution of electrons over the energy states of the semiconductor. In an *n*-type semiconductor (in which electrons are the mobile carriers of charge), the Fermi level is situated close to the edge of the conduction band; correspondingly for *p*-type semiconductors (in which holes are the mobile carriers), it lies close to the edge of the valence band. When the semiconductor is in thermal equilibrium, the Fermi energy is constant throughout the whole crystal. If we now consider a crystal that contains an *n*-type and a *p*-type region, it would have an energy band diagram as shown in Fig. 4a. At equilibrium, there is a difference of potential between the conduction band electrons on the *n* and *p* side of the "*p-n* junction." This potential difference (E_B) is a barrier to charge carriers trying to cross the junction.

If an external voltage is applied such that the potential difference between the *n* and *p* sides is lowered, the flow of current across the junction via holes and electrons is greatly enhanced. A junction in this condition is said to be biased in the forward direction (Fig. 4b). Since there can be no appreciable buildup of charge in either the *n*- or *p*-type regions, the increase in the forward current leads to a proportional increase in the rate of recombination. The current (J) through a *p-n* junction is given by the relation:

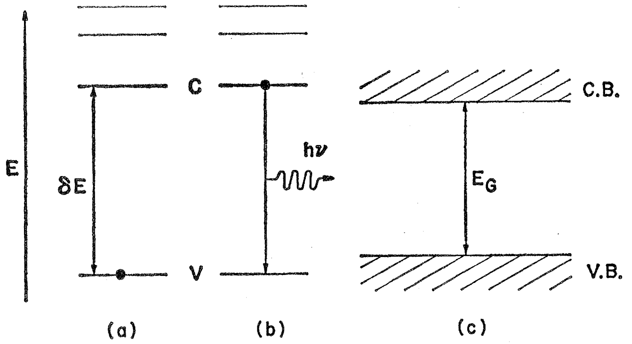
$$J = J_0 \exp\,(V/\beta kT)$$

where V is the applied voltage expressed in electron volts, T is the temperature, and β is a constant whose value depends on the nature of the recombination mechanism. It is this type of junction where holes and electrons recombine which, in principal, can have an efficiency approaching 100 percent in converting electrical energy into electromagnetic radiation. Such efficiencies have in fact been realized in gallium arsenide, where the emitted radiation is in the near-infrared region of the spectrum (*1*). The *p-n* junction is not the only structure which converts electrical energy into light; but so far it is one of the most favorable, and we will therefore confine our discussion to it.

The conversion of electrical energy into light is the result of radiative recombination of electrons and holes. The efficiency of this process is the ratio of the rate of radiative to the total (radiative plus nonradiative) recombination. The simplest possibility is band-to-band recombination; that is, the direct recombination of a free electron with a free hole. In some cases this recombination occurs through intermediate states known as exciton states. The second possibility involves a shallow electronic state (Fig. 5). In this case an electron is first trapped by a donor atom and subsequently recombines directly with a hole or with a hole trapped on a shallow acceptor level. The photon energy generated in this recombination process will be somewhat smaller than that of the band-to-band recombination. Photons with substantially smaller energies are generated when deep-lying electronic levels are involved, as illustrated by the third recombination possibility (Fig. 5) for the case of a deep-lying donor.

There is no sharp limit on the long wavelength side for the possible emission, but at high energy or short wavelength, the bandgap of the semiconductor imposes certain limitations. For the diode to emit visible radiation, E_G has to be greater than approximately 1.7 electron volts. Although many compounds meet this criterion, most are not good semiconductors. A few meet both criteria, and they are listed in Table 1.

To be useful in a *p-n* junction light



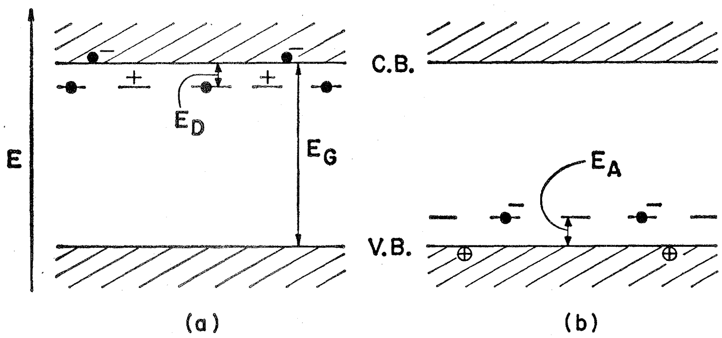
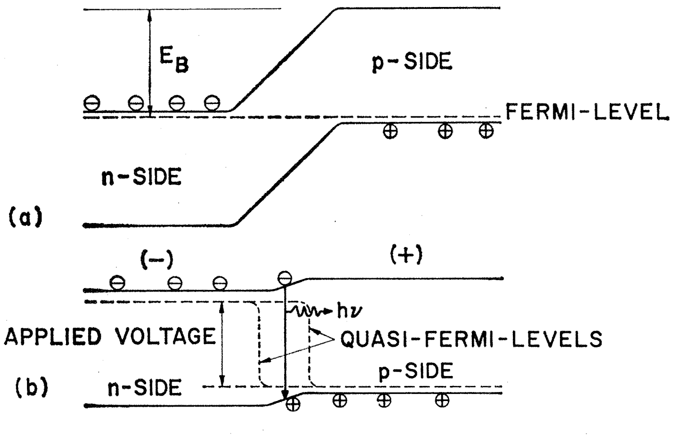


Fig. 2 (left). Electronic energy states of (a) an isolated atom with electron in ground state; (b) an isolated atom with electron in first excited state; and (c) a solid with the states forming the conduction band (*C.B.*) and the valence band (*V.B.*). Fig. 3 (right). Schematic energy diagram for (a) an *n*-type semiconductor and (b) a *p*-type semiconductor.



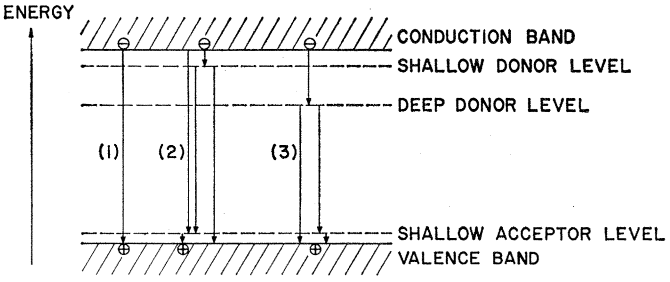


Fig. 4 (left). Typical *p-n* junction under (a) equilibrium and (b) forward-bias conditions. Fig. 5 (above). Scheme of the pertinent energy bands and impurity levels as well as possible recombination paths.

source, it must be possible to "dope" the material (introduce impurity atoms) so that it behaves as both an *n*-type and a *p*-type semiconductor. Most compounds of the group III and V elements (like aluminum phosphide and aluminum arsenide) fulfill this requirement. Similarly, silicon carbide (SiC), a compound of the IV-IV group, qualifies. Compounds of the elements of groups II and VI (like zinc sulfide and zinc oxide), however, do not meet this criterion, because they are limited by conductivity type. Another requirement is the stability of the material. Compounds of aluminum, such as aluminum arsenide and aluminum phosphide, tend to decompose in a normal moist-air environment. The initially small number of candidates in Table 1 is thus further reduced. In addition to the foregoing criteria, one must consider the all-important problems involved in growing single-crystals with controlled concentrations of impurities. At present, there are only two potentially useful binary compounds, gallium phosphide and silicon carbide, and two ternary systems consisting of solid solutions of GaP–GaAs and AlAs–GaAs. In any case, in order to reproduce dependable semiconductor light sources, the preparation of properly doped and otherwise defect-free material is mandatory.

The type of optical transition in each material depends on the valence and conduction band structure of the compound. When the minimum in the conduction band occurs (in momentum space) at the same value as the maximum of the valence band, a transition between a thermalized free electron and a thermalized free hole is called a direct transition. It occurs without the assistance of a phonon. Such transitions take place rapidly and are, in general, more efficient than indirect transitions. As an example of a direct transition, the energy-band structure of gallium arsenide (GaAs) is shown in Fig. 6a. Direct transition materials have the advantage that the efficiency of radiative recombination increases with an increase in the excitation. As more current is passed through the diode, the nonradiative processes are overwhelmed. Many of the potential wide bandgap semiconductors like gallium phosphide have indirect optical transitions (Fig. 6b). In order that a free thermalized electron recombine with a free thermalized hole, the transition must be assisted by the emisson or absorption of a phonon to conserve momentum. This requirement leads to a long lifetime, and, therefore, other recombination processes which may not require phonon assistance may dominate. In these other processes, one or both of the charge carriers are first bound to impurity states. Some of the processes lead to radiative and others to nonradiative transitions. Whenever there is a competition between radiative and nonradiative processes in indirect bandgap materials, the nonradiative processes dominate at room temperature (about 300°K), and the radiative processes at lower temperature (less than 77°K).

For the application of an efficient visible semiconductor light source, the operating temperature would preferably be at 300°K. In order to achieve a high efficiency in the wider indirect bandgap semiconductors, an impurity that binds the minority or injected carrier very tightly is required. In addition, the subsequent recombination process must be radiative. The value of the binding energy should be large, relative to the thermal energy at 300°K, which is about 0.025 electron volt. Since an injected charge carrier, trapped at a deep electronic state, is not readily ionized or excited, it will result in a radiative transition. Such a center has recently been identified in gallium phosphide (*2*). The center, however, is not simple, but consists of two atomic defects substituted on adjacent lattice sites. The complex

Table 1. Some characteristics of well-known semiconductor materials.

Material	Bandgap energy	Wavelength* (Å)	Doping	Quantum efficiency (% obs.)
		Indirect transition		
SiC	2.2 to 3.0	5630 to 4130	*n*, *p*	~10^{-2} (5600 Å)
GaP	2.24	5540	*n*, *p*	~2 (7000 Å) ~10^{-2} (5800 Å)
		Probably indirect transition		
AlAs	2.3	5400		
AlP	2.4	5170	*n*, *p*	
BP			*n*, *p*	
		Direct transition		
$GaAs_xP_{1-x}$	~1.9	~6600	*n*, *p*	0.1 (6600 Å)
$Al_xGa_{1-x}As$	~1.75	~7100	*n*, *p*	3 (7300 Å)
ZnS	3.6	3450		
ZnO	3.3	3760	*n*	
ZnSe	2.7	4600	*n*	
CdS	2.41	5150	*n*	
ZnTe	2.26	5490	*p*	
CdSe	1.67	7430	*n*	
CdS_xSe_{1-x}			*n*	
$ZnSe_xTe_{1-x}$			*n*, *p*	
$Zn_xCd_{1-x}Te$			*n*, *p*	

* Approximate maximum at 300°K.

consists of an oxygen atom (donor) substituted on a phosphorus site next to a zinc atom (acceptor) on a gallium site. The complex has a binding energy for an electron of about 0.3 electron volt and a hole-binding energy of about 0.037 electron volt. These complex centers are formed when oxygen as a minority impurity is incorporated along with zinc as the majority impurity on the *p* side of the junction. Only some of the oxygen atoms will be associated with a neighboring zinc atom. The actual number of associated oxygen atoms can be optimized by annealing at about 600°C (*3*). The association occurs because of the coulombic attraction of the positive charged oxygen donor and the negative charged zinc acceptor.

Efficient radiative recombination is obtained from the *p* side of the junction when electrons are injected across the junction into the *p* region where the concentration of the zinc-oxygen centers is maximized (*4*). The emission occurs in the red region of the spectrum with the peak intensity at about 7000 Å. Since the emitted radiation is considerably less than E_G, there is little reabsorption after the radiative transition has occurred. An important criterion for a light source is the external quantum efficiency, that is, the number of photons escaping from the semiconductor. The number of photons generated by the total number of recombinations is, in general, considerably higher than those escaping.

The difference between the number of photons generated and those emitted is lost owing to absorption within the semiconductor, and the amount of absorption is proportional to the path length of the photon. The minimum path length is the distance from the point of recombination to the nearest surface of the diode crystal. The photon is then either transmitted and observed externally, or it is reflected. The number of photons transmitted depends on the difference between the indices of refraction of the crystal and the external medium (air). When the two indices match, the transmission is unity. Unfortunately, the index of refraction of semiconductors is usually considerably higher than that of air ($n_{\mathrm{air}} = 1$) so that photons pass through the crystals many times before being transmitted. Thus, the longer the path length, the greater the absorption loss.

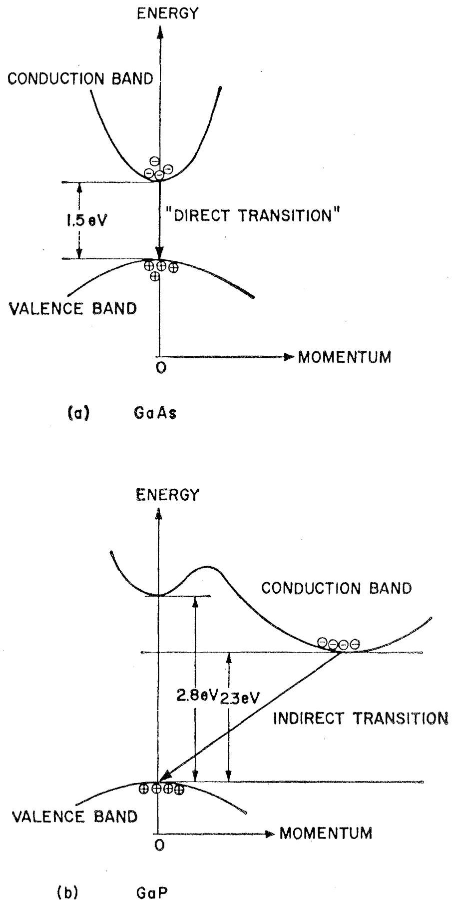


Fig. 6. Energy as a function of momentum for (a) gallium arsenide, direct transition, and (b) gallium phosphide, indirect transition.

The absorption per unit distance in the semiconductor is also dependent on wavelength. Absorption is strong when the photon energy corresponds closely to the energy gap of the crystal. Absorption then goes through a minimum as the photon energy decreases. Beyond the minimum, absorption due to free charge carriers leads again to increased absorption. The red emission in gallium phosphide (GaP) occurs close to the minimum, so that the absorption losses are relatively small, although even for this case the number of emitted photons is approximately one-fifth of the total number of photons generated (*5*). Recombination by way of zinc and oxygen centers in gallium phosphide, with an intensity peak at about 7000 Å, has yielded external efficiencies of up to 2 percent at 300°K (*6*).

A common method of improving the external quantum efficiency is the imbedding of diodes in a clear epoxy resin. This technique raises the number of photons being transmitted at the interface between the crystal and the epoxy resin. The condition for improvement of efficiency is that the epoxy resin must be completely transparent to the emitted photon energy.

Gallium phosphide light-emitting diodes (LED's) have also been prepared with emission occurring in the green region of the spectrum, but the best efficiences in these diodes are at or below 1.5×10^{-2} percent (*7*). The emission of silicon carbide diodes is more in the yellow spectral region with efficiencies up to about 10^{-2} percent. Silicon carbide, like gallium phosphide, is a material in which the optical transitions are indirect. The highest external efficiency at 300°K in these indirect transition materials is 2 percent. Most of the recombination therefore occurs via nonradiative paths. One of the most interesting and important areas of research concerns the understanding and elimination of the mechanism by which the nonradiative recombination occurs. So far, however, little if any progress has been made in this direction.

There are two alloy systems which have shown relatively efficient diode emission. Solid solutions of $\mathrm{Ga}_{1-x}\mathrm{Al}_x\mathrm{As}$ and $\mathrm{GaAs}_{1-x}\mathrm{P}_x$ can be prepared in a composition range of *x* where the alloys have direct optical transitions which are in the red spectral region. $\mathrm{Ga}_{1-x}\mathrm{Al}_x\mathrm{As}$ diodes have been prepared with 300°K-emission efficiencies as high as 3.3 percent at 7300 Å (*8*). Similarly, LED's made from $\mathrm{GaAs}_{1-x}\mathrm{P}_x$ have been measured with efficiencies of 1 percent at 300°K at the very edge of the visible region (*9*). Since the recombination in these alloys is believed to occur via band-to-band transitions, the internal efficiencies may be considerably higher. The emission of these diodes can be shifted toward shorter wavelength (more toward the green spectral region) by increasing the composition variable *x*. Unfortunately, the optical transitions then become indirect, and these alloys suffer from the same limitations as the compounds GaP and SiC; that is, their efficiencies drop.

Visible light sources from light-emitting semiconductors have not been produced on a large-scale production basis although LED's of $\mathrm{GaAs}_{1-x}\mathrm{P}_x$, GaP, and SiC are commercially available. There are two general methods that are used for the preparation of the *p-n* junction in the laboratory. Both processes consist of the preparation of a *p*- or *n*-type substrate wafer (flat crystal plate). In one of the methods, an appropriate impurity is diffused partially into the substrate, so that in the diffused region the conductivity type is changed from *p* to *n* or vice versa, depending on the initial conductivity type. The interface between the unchanged substrate and the inverted region is the *p-n* junction. In the other technique, an epitaxial layer is grown onto the substrate wafer either from the vapor phase or from solution. The epitaxial layer includes an impurity which makes the conductivity of the layer opposite to that of the substrate. To complete the fabrication of a light-emitting diode, metal contacts are provided to the *n* and *p* sides of the junction, and the wafer is diced into the individual diodes. For example, a red-emitting gallium phosphide LED (Fig. 7) has a junction area of about 2×10^{-3} cm^2. Light-emitting diodes, however, can be made either smaller or considerably larger. The diode shown in Fig. 7 operates with an applied voltage of about 2.3 volts at a current of 10 milliamperes with an efficiency of 0.5 percent. The emission spectrum of this diode is shown in Fig. 1.

The development of LED's is still in its embryonic stage. Consequently, the possible applications have not been fully realized. Semiconductor LED's can most obviously be used as indicator lights. At present, this would mainly include equipment with the functional parts consisting of solid state circuits. The advantage of LED's here is mainly the compatibility of the voltages and currents required with the existing circuits, as well as the low-power consumption of the solid state light sources. Typical equipment where LED's would be useful includes computers, telephones with illuminated buttons, cameras (for sound tracts), and "on" lights in portable electronic apparatus such as radios and tape recorders. Other indicator light applications could be in automobiles (dashboard for high beam or directional lights), appliances, illuminated doorbell buttons, indicators in cockpits, and many less common applications such as in space ships and research equipment. Because LED's have greater shock resistance than conventional tungsten bulbs they should offer special advantages in equipment such as aircraft and spaceships.

In principle, semiconductor light sources are not likely to fail catastrophically. The half-life for LED's is the time in which the light output for a fixed input power is reduced to half of its original value. If LED's are to replace conventional lights, their half-life should be in the range of thousands of hours; in fact, 100,000 hours is not an unrealistic goal. With such lifetimes, the indicator lamps would, in many cases, outlive the rest of the equipment.

Solid state light sources may also be used for displays of information, either as a digital or an alphanumeric readout. In the simplest form, seven diodes can be arranged in a figure-eight configuration. With each diode separately addressable, the ten basic numbers can be generated. A more complex application would be an optical display resulting from a great number of diodes in an *x–y* matrix. If each of these is separately addressable, one can now go beyond an alphanumeric message to the display of an optical image. Conceivably, an *x–y* matrix might replace the cathode ray tube and screen in the television sets of the future.

Applications to communication systems and data transmission are possible, but here it is not necessary to use diodes that emit visible light. In fact, LED's emitting longer wavelengths are more desirable. Experimental communication links have been built with LED's emitting coherent radiation in the infrared region of the spectrum.

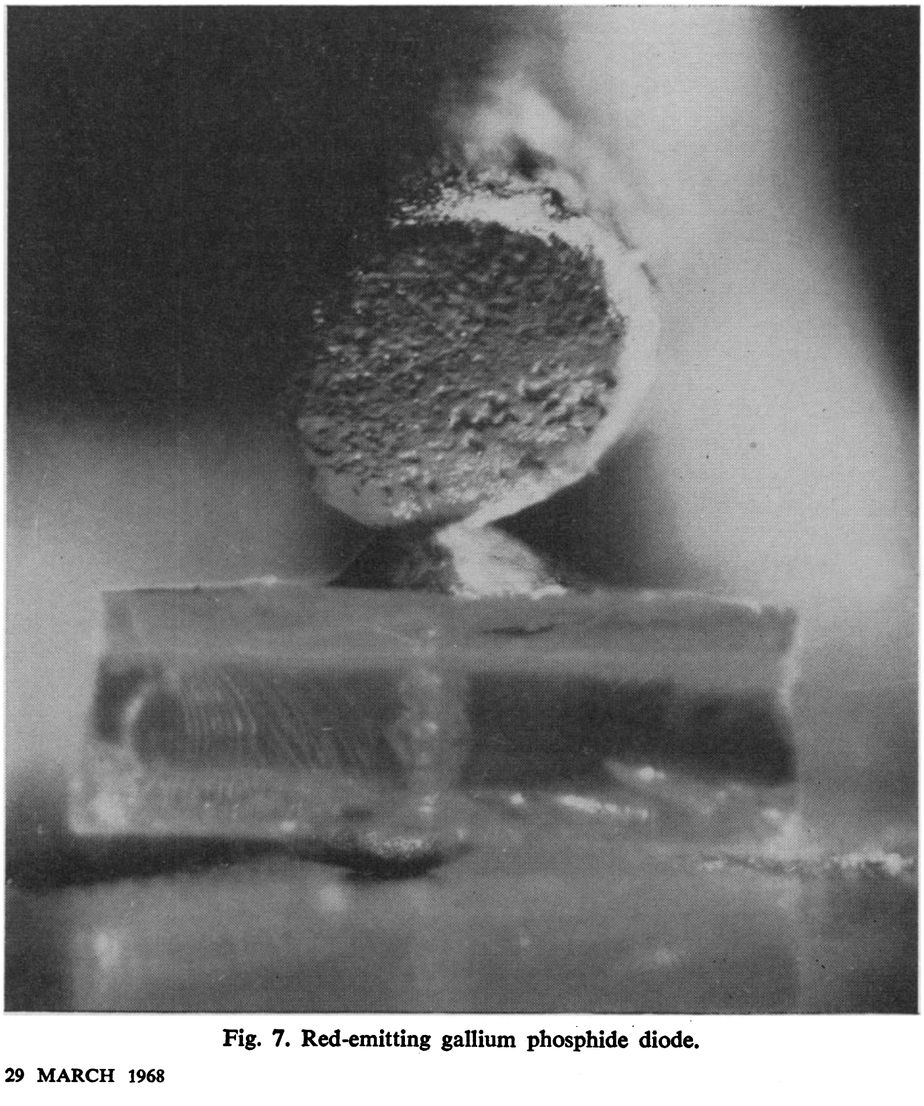


Fig. 7. Red-emitting gallium phosphide diode.

Summary

Electroluminescence from semiconductor diode light sources can occur as a result of the application of a direct current at a low voltage to a suitably doped crystal containing a *p-n* junction. In recent years, it has become apparent that in some materials the efficiency of conversion of electric energy to visible light can be appreciably high. Since light-emitting diodes are compatible with the present electronic circuitry, they have many potential applications.

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