NUMBER 40
OCTOBER 1, 1979

This Week's Citation Classic

Logan R A, White H G & Wiegmann W. Efficient green electroluminescent junctions in GaP. *Solid-State Electron.* **14**:55-70, 1971. [Bell Telephone Laboratories, Murray Hill, NJ]

A description is presented of the growth procedures used to form efficient green light emitting diodes in Gallium Phosphide. The electroluminescent efficiency increases linearly with the concentration of nitrogen in the crystal. The controlled incorporation of nitrogen atoms into the crystal is described and other junction design factors influencing the efficiency are discussed. [The *SCI*® indicates that this paper has been cited over 90 times since 1970.]

Ralph A. Logan
Bell Laboratories
Murray Hill, NJ 07974

January 8, 1979

"The popular hand held calculator is an excellent example of the compatibility of light emitting diodes (LEDs) used in the read out with the p-n junctions, transistors, and integrated circuits used in the processor. Actually the LED is also just a p-n junction, not made of silicon (Si) as in most of the calculator components, but made of another semiconductor such as gallium arsenide phosphide (GaAsP) and operating at similar levels of current and voltages as the transistors, etc The basic difference in these two semiconductors is the energy gap: the energy that an electron loses when it drops from a conducting or free state to recombine with an empty state or hole in the valence band. Since the photon energy cannot exceed the energy gap, in Si with a 1.1 eV energy gap, this recombination radiation energy is in the infrared, but in GaAsP this radiation is visible photons and depending upon the crystal composition could emit green light in GaP where the energy gap is 2.4 eV.

"With the objectives of better understanding and greater efficiency of solid state light sources, a research program was started at Bell Laboratories about 20 years ago to explore the properties of GaP. Dr Murray Gershenzon (now at the University of Southern California) was the first scientist at Bell Laboratories to work on GaP. By the late 1960s several scientists here (and in other laboratories) were studying the growth, purification, and spectroscopy of GaP. In the third area, a great deal of effort was expended by Dr. David G. Thomas and his co-workers to correlate the luminescence properties of the crystals with the controlled amounts of "impurities added to the crystals during growth. In particular, they discovered that crystals containing both zinc and oxygen at levels of a few PPM were highly luminescent[1,2] Zinc and oxygen together formed a recombination center such that when free carriers were created by high energy photons (ultra violet), about 11% of the injected carriers recombined, emitting photons with energy of 1.8 eV (red light). This process is comparable in efficiency to small incandescent light bulbs. In 1967, working with Dr. F. Trumbore and H. G. White, we incorporated this mechanism into p-n junctions to generate red luminescence at an efficiency of 2%.[3] This was obviously a potentially useful commercial device and a group outside the research area was formed to explore the development of LEDs.

"I then was encouraged to look into the possible generation of green luminescence in a similar junction By removing the oxygen impurity in the junction growth, the red luminescence was minimized and the other background luminescent processes could be observed. Occasionally this background luminescence was predominantly green with a photon energy characteristic of recombination on nitrogen impurities, a recombination mechanism that Dr. David Thomas and his co-workers had shown was an efficient recombination mechanism at low temperatures. [4]

"Nitrogen was added to the junction crystals by performing the growth in a hydrogen ambient containing a partial pressure of ammonia gas and a dramatic increase in the green luminescence was achieved In fact, the green LEDs were brighter than our red ones. The careful control of residual impurities and the techniques of forming the junction by adding impurities from the gas stream that we described are still used today.

"A red signal light historically denotes trouble or danger. However, the green LED does not have this connotation and is a basically useful lamp for many purposes. It is presently widely used in the Bell System to light the dial and as signal lamps in telephone handsets with pushbuttons, powered only from the same central office source that operates the telephone instead of from a separate electrical outlet previously required Other important communications applications include key telephone and private branch exchange (PBX) systems where LEDs are used in button switches, indicators, and maintenance aids. An impressive additional feature of these LEDs is their longevity, with operating lifetime before failure exceeding 50 years "

1. **Thomas D G, Gershenzon M & Trumbore F A.** *Phys. Rev. A* **133:** 269-79, 1964.
2. **Gershenzon M, Trumbore F A, Mikulyak R M & Kowalchik M.** *J. Appl. Phys.* **36**:1528-37, 1965.
3. **Logan R A, While H G & Trumbore F A.** *Appl. Phys. Lett.* **10**:206-8, 1967.
4. **Thomas D G, Hopfield J J & Frosch** C J. *Phys. Rev. Lett* **15**:857-60, 1965.