Table I. The Verdet Constant in Minutes/(Oe-cm) of the 58% Terbia Glass at Several Temperatures.

| $T$ °K | $V$ |
|---|---|
| 287.9 | 0.313 |
| 272.2 | 0.331 |
| 75.3 | 1.195 |
| 3.935 | 14.27 |
| 2.08 | 22.43 |

length. Presumably, their temperature was about 300°K.

Our attention has been called to the work of Borrelli[10] who has observed that the Verdet constant is very nearly proportional to the rare-earth ion concentration $N$. His measurements on $Tb_2O_3$–doped soda-silicate glass indicates $dV/d(1/T) \approx 27$ min-°K/(Oe-cm), whereas our results in Table I indicate $dV/d(1/T) \approx 90$ min-°K/(Oe-cm). If $V = C_BN$, where $C_B$ = Borrelli's constant for the doped soda-silicate glass, we might expect to find $N = 110 \times 10^{20}$ Tb ions/cm$^3$ for our sample. Actually, however, based on the measured density of 4.59, the 58% by weight of $Tb_2O_3$, and the silica-to-alumina weight ratio of 2.08, we calculate an $N$ of only $88 \times 10^{20}$ Tb ions/cm$^3$. This disagreement between expected and actual ion densities is not large enough to cause concern for two reasons: First, the host in our glass, alumina-silica, presents a different average Tb ionic environment than in the case of the soda-silicate glass; thus $C_B$ can be expected to be different in the two glasses. Second, when the ion density gets large enough so that the glass is antiferromagnetic it is probable that $V$ is no longer linear in $N$.

To summarize, we have measured the Faraday effect in an alumina-silicate glass containing 58% by weight of terbia. We find this useful glass to be antiferromagnetic with a Curie temperature of −1.16°K. Since this is relatively small, the behavior of the Verdet constant at higher temperatures closely resembles that of a simple paramagnetic solid.

[1] J. Becquerel and W. J. De Haas, *Proc. Acad. Amsterdam* **32,** 578 (1929); **32,** 590 (1929); **32,** 1199 (1929); **32,** 1206 (1929); J. Becquerel, *Proc. Acad. Amsterdam* **32,** 749 (1929).

[2] J. van den Handel, *Encyclopedia of Physics* (Springer-Verlag, Berlin, 1956), Vol. 15, p. 1.

[3] P. B. Alers, *Phys. Rev.* **116,** 1483 (1959).

[4] P. B. Alers, *Phys. Rev.* **105,** 104 (1957).

[5] W. De Sorbo and W. A. Healy, *Cryogenics* **4,** 257 (1964); J. D. Livingston and W. De Sorbo, General Electric Research Laboratory Report No. 66-C-328, September 1966.

[6] K. J. Carroll, D. H. Liebenberg, and W. C. Overton, *Rev. Sci. Instr.* **38,** 260 (1967); K. J. Carroll, *Phys. Lett.* **23,** 416 (1966).

[7] C. C. Robinson and R. E. Graf, *Appl. Opt.* **3,** 1190 (1964).

[8] C. C. Robinson, private communication.

[9] H. L. Laquer, *Proceedings of the International Conference on High Magnetic Fields* (edited by H. Kolm et al., MIT Press and John Wiley & Sons, 1962), p. 156; H. L. Laquer and E. F. Hammel, *Rev. Sci. Instr.* **28,** 875 (1957).

[10] N. F. Borrelli, *J. Chem. Phys.* **41,** 3289 (1966); *Proc. of VII International Congress on Glass*, Vol. 1, Brussels, 1965.

# EFFICIENT VISIBLE ELECTROLUMINESCENCE AT 300°K FROM $Ga_{1-x}Al_xAs$ *p-n* JUNCTIONS GROWN BY LIQUID-PHASE EPITAXY

*H. Rupprecht,* J. M. Woodall,* and G. D. Pettit*
IBM Watson Research Center
Yorktown Heights, New York
(Received 19 June 1967)

Efficient visible light emitting diodes have been fabricated from $Ga_{1-x}Al_xAs$. Epitaxial layers were obtained by a modified solution growth technique. External quantum efficiencies of up to 3.3% have been measured at room temperature on diodes, which had their emission at 1.70 eV. The switching time for the light emission at 300°K was measured to be 60 nsec.

In this Letter, a modified liquid-phase epitaxial technique will be described which allows the fabrication of efficient visible light emitting diodes in $Ga_{1-x}Al_xAs$. Values for the total external quantum efficiency at 300°K of up to 1.2% were observed for current densities of 50 A/cm$^2$. The peak emission occurred at 1.70 eV. If the same set of diodes is coated with an epoxy, to reduce internal reflections, external quantum efficiencies of up to 3.3% are measured under dc operation at comparable current densities.

*The work of these authors was supported by the U.S. Army Electronics Command, Ft. Monmouth, N. J.

The method used for preparing the epitaxial layers is a modification of the technique developed by Nelson.[1] It permits the formation of the *p-n* junctions in a single-step cooling cycle at a controllable distance from the physical boundary of the GaAs substrate by means of counterdoping the solution. To accommodate the $Ga_{1-x}Al_xAs$ system, a vertical apparatus was used similar to the one described in ref. 2. It contained an $Al_2O_3$ crucible loaded with Ga, Al, excess GaAs and an *n*- or *p*-type dopant (Te or Zn). The epitaxial layers were deposited on GaAs substrate wafers with faces perpendicular to the ⟨100⟩ direction and which were mounted on a graphite holder. High purity forming gas was passed through the system during growth. The layers were deposited during cooling of the apparatus from 1000°C to 880°C. For this temperature range, the composition of the layers was found to depend on the ratio of Ga to Al in the melt and on the cooling rate. The growth was terminated by removal of the graphite holder from the melt at the end of the cooling cycle. The regrown layers were usually about 100 $\mu$ thick and were extremely homogeneous in their composition. Electron microprobe measurements showed that the variation in the Ga-Al ratio is less than 2% along the growth axis. For high quantum efficiencies of the near-edge luminescence, it is desirable to stay within a composition range of direct band gap material.[3] In addition, it is desirable to have the highest photon energy emitted from such a direct material, as the eye sensitivity rapidly increases with increasing photon energy in that range. Therefore, shallower impurity levels as given by Zn and Te are preferable. All optical and electrical properties discussed in the following section were obtained from diodes containing Zn and Te. These diodes had all four sides cleaved and had been shaped to parallelopipeds.

One important result is that the influence of deep lying, competitive recombination centers has been markedly reduced by the use of the liquid-phase epitaxial technique, compared to vapor growth methods.[4] Figure 1 gives the spectral distribution for a typical set of diodes. At 300°K, about 86% of the externally observable photons are concentrated in a high energy line of about 90 MeV width. Its peak centers at 1.70 eV. With decreasing temperature, the emission intensity increases. For the most efficient diodes, the quantum efficiency of the main peak increased by a factor of about eight when the temperature was decreased from 300°K to 77°K. At 77°K the relative intensity of the low energy emission is greater than at 300°K. Even so, only about 26% of the total number of photons is distributed over essentially two lines with peak energies of 1.5 eV and 1.28 eV. The dominant high energy line at 77°K has a peak at 1.79 eV. At room temperature, the emission intensity is superlinear for current densities less than 50 A/cm². For higher values it becomes linear. At 77°K, however, a practically linear behavior was found for current densities varying from 0.05 A/cm² to 50 A/cm². This upper limit was chosen only with regards to the series resistance in our structures. The series resistance for a typical diode is 50 Ω at 300°K and increases to 120 Ω at 77°K. At 300°K as well as 77°K it was found that the diode current depended on applied voltage such as

$$I = I_0 \exp \frac{V}{\beta kT}$$

with $\beta \approx 2$. This is similar to observations made for GaAs and GaP.[5,6] The switching time for these light emitting diodes was found by K. Konnerth to be about 60 nsec.

As mentioned previously, the composition of the epitaxial layers depends on cooling rate and melt composition. Figure 2 gives the peak energy of the high energy line as a function of the Al-Ga ratio in the melt for constant cooling rate. There appears to be a kink in the data at about 1.9 eV, indicating the

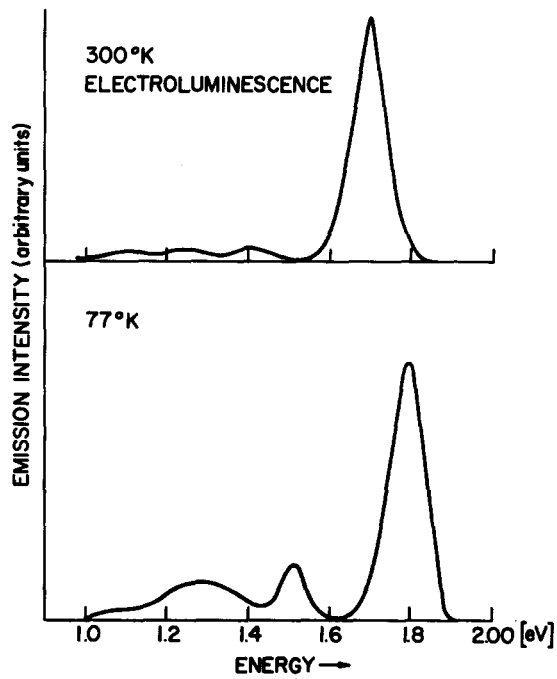


**Fig. 1. Spectral distribution of the electroluminescence in $Ga_{1-x}Al_xAs$ diodes (measured with a PbS cell).**

transition from direct to indirect energy band structure in the material, which is in agreement with experimental data reported by Ku and Black[4] and with a linear interpolation of the GaAs–AlAs series by Hilsum.[7]

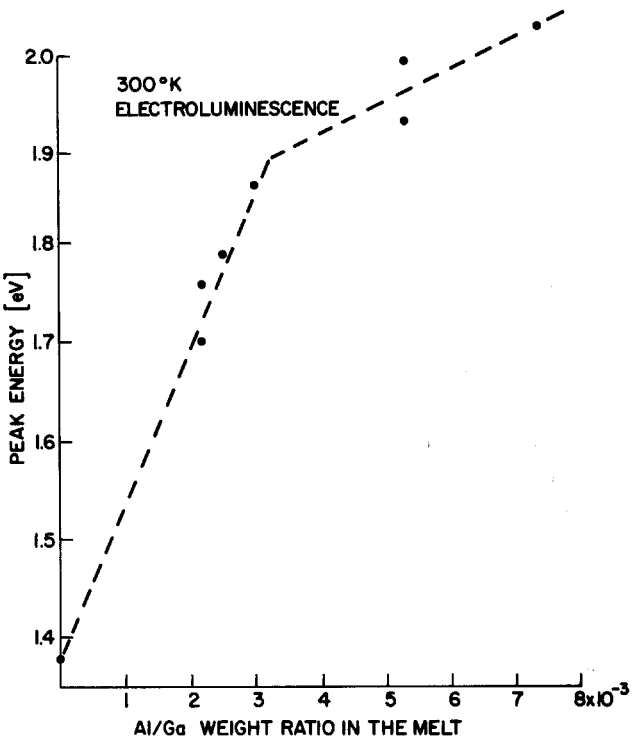


**Fig. 2. The energy peak of the high energy line as a function of the Al-Ga ratio in the melt.**

Summarizing our results, we have found that liquid-phase epitaxy is well suited for preparing layers of $Ga_{1-x}Al_xAs$ on GaAs substrates. In contrast to results by Ku and Black[4] for vapor-phase epitaxy, we have been able to grow homogeneous layers of about 100 $\mu$ in thickness. Problems due to deep lying, competitive recombination centers as encountered by Ku and Black, have been drastically reduced, resulting in efficient visible light emitting diodes.

It is a pleasure to thank many of our colleagues who contributed to this work. Stimulating discussions with Drs. M. I. Nathan, A. H. Nethercot and F. Stern are gratefully acknowledged. The chemical analysis was carried out by Dr. W. Reuter and J. Kuptsis. We also thank E. H. Bayer, V. Garrison, C. J. Lent and W. C. Wuestenhoefer for technical assistance.

[1] H. Nelson, *RCA Rev.* **24,** 603 (1963).
[2] H. Rupprecht, *Proc. 1966 Symp. on GaAs, Reading* (Institute of Physics and Physical Society, London, 1967), p. 57.
[3] M. Pilkuhn and H. Rupprecht, *J. Appl. Phys.* **36,** 684 (1965).
[4] S. M. Ku and J. F. Black, *J. Appl. Phys.* **37,** 3733 (1966).
[5] M. Pilkuhn and H. Rupprecht, *J. Appl. Phys.* **38,** 5 (1967).
[6] M. R. Lorenz and M. Pilkuhn, *J. Appl. Phys.* **37,** 4094 (1966).
[7] C. Hilsum, *Proc. 7th International Conference on Physics of Semiconductors, 1964* (Dunod, Paris, 1964), p. 1127.

# CARRIER GENERATION AND SWITCHING PHENOMENA IN *n*–GaAs DEVICES

*H. W. Thim and S. Knight*
Bell Telephone Laboratories, Inc.
Murray Hill, New Jersey
(Received 18 May 1967)

By measuring the steady-state potential distribution in *n*–GaAs samples with ohmic contacts, very high electric fields have been found near the anode contacts. In samples with $n \cdot L$ (carrier concentration × sample length) products greater than $10^{12}$ cm$^{-2}$, switching from the Gunn mode to a high current, lower (constant) voltage state takes place along with the appearance of a high field at the anode. In samples with $n \cdot L$ products less than $10^{12}$ cm$^{-2}$ the buildup of the high field is accompanied by a sudden increase in current. These high currents are due to carrier generation in a narrow region near the anode.

Switching associated with a current-controlled negative resistance effect has been observed in bulk single-crystal *n*–GaAs by Hakki,[1] Liu,[2] and Copeland.[3] Liu proposed that this phenomenon could be explained on the basis of impact ionization as discussed by Gunn[4] and Steele et al.,[5] taking place in a localized high-field region near a contact. Copeland[3] and Conwell[6] suggested that the phenomenon could be the result of low field avalanche occurring uniformly throughout the sample. The purpose of the present experiment was to determine the field distributions in devices before and after switching occurs. The results discussed in the following sections indicate that carrier generation can occur in a narrow high-field region near the anode.

Potential profile measurements using a point con-