

## Electroluminescence of AlN

G. A. WOLFF, I. ADAMS, AND J. W. MELLICHAMP

United States Army Signal Research and Development Laboratory, Fort Monmouth, New Jersey

(Received January 12, 1959)

Electroluminescence in the visible region is observed when AlN is excited by either ac or dc. The emitted spectra consist of narrow bands in the 400–500  $m\mu$  region and broad continuous bands in the 500–700  $m\mu$  region. The broad bands vary according to the activator agents. With ac, the luminescence is in phase with the applied voltage. With dc, light is emitted in the vicinity of the cathode and decays with time. This decay can be explained by polarization. The presence of a barrier at the cathode is indicated. Impact excitation is proposed.

### INTRODUCTION

ELECTROLUMINESCENCE in the visible region has been observed in BN,<sup>1</sup> GaP,<sup>2,3</sup> Ga(P, As), and (Ga, In)P.<sup>4</sup> Other III-V compounds, such as GaN and AlN show the same effect. GaN, prepared by thermal decomposition of (NH<sub>4</sub>)<sub>2</sub>GaF<sub>6</sub>,<sup>5</sup> or by the reaction of Ga,<sup>6</sup> (GaCl<sub>3</sub> or GaP with NH<sub>3</sub> at elevated temperatures, shows a bluish-white electroluminescence which is low in intensity. Efforts were concentrated on AlN<sup>7</sup> to determine whether or not this material could be made to emit a brighter luminescence than that produced in GaN. Experimentation has shown that this can be accomplished. Observed light intensity compares favorably with that of ZnS.

### EXPERIMENTAL DATA

AlN is prepared by the reaction of high-purity Al<sup>8</sup> with N<sub>2</sub> at high pressure and temperature. The hard sintered mass formed by this reaction is first ground to a powder, treated with Cl<sub>2</sub> to remove excess Al and other impurities, and then activated with a Group II element, or with Cu or Mn. Luminescence is produced when the activated material is placed between two electrodes and either ac or dc is applied.

The luminescent spectra were photographed on Eastman 103f film in the 400–700  $m\mu$  spectral region. In the 400–500  $m\mu$  region, the spectrograms show what appear to be lines, and in the 500–700  $m\mu$  region broad continuous bands are seen. The lines in the 400–500  $m\mu$  region are, in fact, a series of narrow bands identified from data by Pearse and Gaydon<sup>9</sup> as the second positive system of N<sub>2</sub>. The same system, observed in the tribo-

luminescent spectrum of arsenic trioxide, was reported previously.<sup>10</sup> Since no electrical sparking is seen in the excitation of the luminescence, it is believed that the N<sub>2</sub> system is excited by no known type of discharge or excitation and, in some cases, is an integral part of the excitation source for the broad bands which are emitted at longer wavelengths. The specific activation agents responsible for these broad bands have not been identified and only a preliminary indication can be given. Spectrochemical analysis shows the purest AlN prepared to be approximately 99.99% pure. This pure material emits predominantly the N<sub>2</sub> system in the 400–500  $m\mu$  region and when activated with a doping agent broad bands then appear in the 500–700  $m\mu$

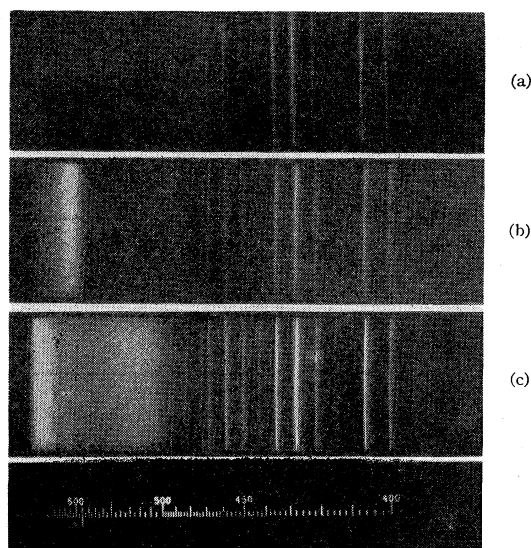


FIG. 1. Electroluminescent spectra emitted from AlN. (a) This spectrum is emitted from 99.99% pure sample. In the 400–500  $m\mu$  region is the narrow band structure of the second positive system of N<sub>2</sub>, and in the 650–700  $m\mu$  region is a broad band. This spectrum is common to all other spectra regardless of the activator. The electroluminescence is blue in appearance. (b) This spectrum is emitted from sample with trace of Mn (0.001%). A broad band is seen in the 600–630  $m\mu$  region in addition to spectrum A. The electroluminescence is red in appearance. (c) This spectrum is emitted from sample activated with a high concentration of Mn (~1.0%). Broad bands appear between 500 and 700  $m\mu$ . Note fine structure in the 650–700  $m\mu$  region. The electroluminescence is green in appearance.

<sup>1</sup> S. Larach and R. E. Shrader, *Phys. Rev.* **102**, 582 (1956); and **104**, 68 (1956).

<sup>2</sup> Holt, Alfrey, and Wiggins, *Nature* **181**, 109 (1958).

<sup>3</sup> Wolff, Hebert, and Broder, *Phys. Rev.* **100**, 1144 (1955).

<sup>4</sup> Wolff, Hebert, and Broder, *Proceedings of the International Colloquium on Semiconductors and Phosphors, Garmisch, 1956* (Interscience Publishers, New York, 1958), p. 547.

<sup>5</sup> H. Hahn and R. Juza, *Z. anorg. allgem. Chem.* **244**, 111 (1940).

<sup>6</sup> Johnson, Parsons, and Crew, *J. Phys. Chem.* **36**, 2652 (1932).

<sup>7</sup> Electroluminescence in AlN has also been mentioned by A. Fischer [*Physik. Verhandl.* **7**, 204 (1957)].

<sup>8</sup> Through the courtesy of Dr. A. Imich and Mr. I. Stelzer, United Mineral and Chemical Corporation, New York, New York.

<sup>9</sup> R. W. B. Pearse and A. G. Gaydon, *The Identification of Molecular Spectra* (Chapman and Hall, Ltd., New York, 1950), p. 169.

<sup>10</sup> Stranski, Strauss, and Wolff, *Z. Elektrochem.* **59**, 341 (1955).

region. Figure 1 shows various electroluminescent spectra of AlN samples.

The efficiency of the electroluminescence of AlN (Mn) was found (with the aid of Williams, Studer, and Roberts) to be  $10^{-3}$  lumens/watt when dc was applied. With ac (60 cps) and the sample either placed in direct contact with the electrodes or separated from them by polystyrene foils, the efficiency was found to be of the same magnitude, although some smaller values have been measured. The two latter values have been determined by photomultiplier measurements using the first value (dc) as a standard.

Pure crystals of AlN obtained by sublimation are found to be neither fluorescent nor phosphorescent.<sup>11</sup> In some crystals a weak electroluminescence was detected. AlN is also found to be relatively weak in electroluminescence when either excess Al or excess doping agent is present or when prepared by another method such as by the thermal decomposition of  $\text{NH}_3 \cdot \text{AlCl}_3$ .<sup>12</sup> Samples which electroluminesce also phosphoresce with the same color. One exception has been found in AlN(Mn) which emits a green electroluminescence but which phosphoresces with a deep blue color. A weak phosphorescence is observed immediately upon removal of the electrical field and persists for about ten minutes. X-ray diffraction patterns reveal traces of  $\alpha\text{-Al}_2\text{O}_3$  in a few samples. To check the possibility of this being the source of the observed electroluminescence and phosphorescence, both pure and doped  $\text{Al}_2\text{O}_3$  were tested. Although a faint, bluish-white electroluminescence in  $\alpha\text{-Al}_2\text{O}_3$  was detected, it was not sufficient to account for the intensity and variety of colors observed in AlN.

The electroluminescence of AlN is emitted from the cathode region, the same as in  $\text{ZnS}^{13-15}$  and GaP.<sup>3</sup> Current and luminescence both decrease with time, probably as a result of internal polarization of the sample. Early samples show the time decay of both current and light to be linear in a log-log plot with a negative slope of 0.2 for current and 0.16 for light. Later samples show only a slight decay. The schematic diagram in Fig. 2 illustrates this behavior. The conducting glass plate and the metal base are electrodes 1 and 2, respectively. During the "forward period" at electrode 2, being cathode, a luminescence of moderate intensity is emitted which slowly decays. A "reverse-period" follows, with electrodes 1 and 2 changing to cathode and anode, respectively. During this period, a short light flash from electrode 2 is followed, within five seconds, by a build-up of a fairly intense light emission at electrode 1. As occurred previously at electrode 2, the luminescence at electrode 1 then slowly decays. Upon a second reversal of

the field, electrode 1 again becomes the anode, and an intense burst of light is emitted at electrode 1, followed by a build-up of luminescence at electrode 2 with subsequent decay, and so on. The burst of light, which appears immediately after the field reversal, is emitted only when the opposing field was applied for a sufficient duration. The current increases rapidly to a peak value and then decays slowly. This occurs during each reversal, following a short delay. Prolonged irradiation with infrared light reduces the current decay after reversal, but has no appreciable influence upon the light decay. Changing the contacts by either moving or lifting the conducting glass plate restores the original behavior. Ultraviolet or  $\gamma$ -irradiation leaves the electrolumines-

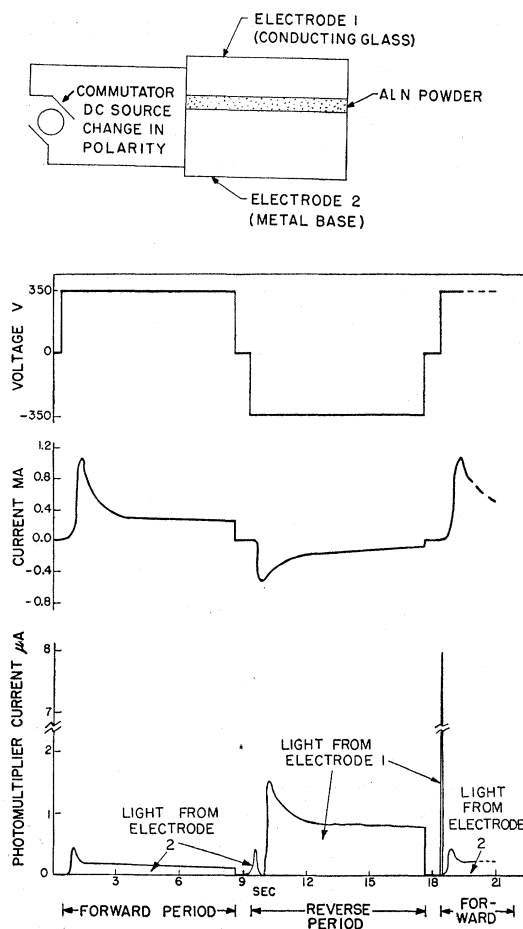


FIG. 2. Schematic diagram showing the change of electroluminescence intensity and current with time as a function of the electric field applied to AlN crystals. These crystals are placed between conducting glass (electrode 1) and a metal plate (electrode 2). Electrode 1 is placed next to the photomultiplier. During the "forward period" electrode 1 and 2 are anode and cathode, respectively; they change accordingly in the next—"reverse"—period to cathode and anode, respectively. Note that the light flash immediately following the first application of a field is not observed. The flash appears only upon field reversal. The scale for the light intensity values (given in photomultiplier current) is broken. A schematic view of the experimental arrangement is shown at the top.

<sup>11</sup> Also see C. Buhner and E. Banks, *Electrochem. Soc. Abstracts*, Spring Meeting, 1958, p. 22.

<sup>12</sup> Tiede, Thimann, and Senses, *Berichte* **61B**, 1568 (1928).

<sup>13</sup> W. W. Piper and F. E. Williams, *Phys. Rev.* **87**, 151 (1952)

<sup>14</sup> W. W. Piper and F. E. Williams, *Suppl. Brit. J. Appl. Phys.* **4**, 39 (1955); *Solid-State Physics* edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1958), Vol. 6, p. 96.

<sup>15</sup> D. R. Frankl, *Phys. Rev.* **111**, 1540 (1958).

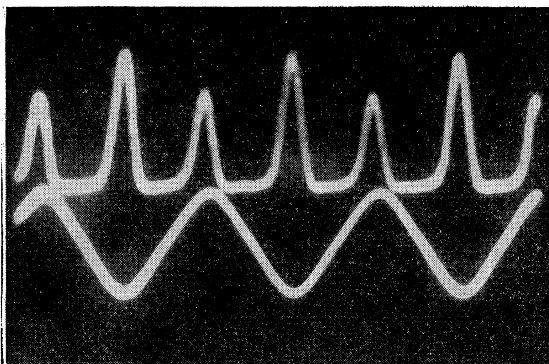


FIG. 3. Oscilloscope of electroluminescence intensity (upper curve) synchronized with the current through the crystal layer (60 cps; lower curve). The current is nonsinusoidal due to the nonohmic characteristic of the crystals. The more intense light is emitted from the electrode 1 which is next to the multiplier.

cence and conductivity of the sample virtually unaffected. In a first approximation, the logarithm of the electroluminescence is a linear function of the inverse square root of the ac voltage. With ac, a slower decrease with time in current, and light is observed. In this case, the light, current, and voltage are in phase up to 2000 cps (Fig. 3).

When the crystals are insulated with mica or polystyrene sheets from the electrode, light is emitted only in the first instance following each field reversal. With ac, voltage and light are in-phase while current and light are out-of-phase (Fig. 4).

#### DISCUSSION

The behavior of the electroluminescence of AlN is explained as follows: Electron multiplication and luminescence is caused by impact excitation, following the acceleration of electrons across the rectifying metal-semiconductor and/or *p-n* barriers.<sup>14</sup> When the dc field is applied, the high-ohmic semiconductor behaves like a dielectric in a condenser, with fair insulation at the anode, and even better insulation at the cathode barrier region. While the current flows, within a few seconds a field is slowly building up at the cathode until at a critical field value impact excitation sets in. The electrons, elevated to the conduction band, recombine with co-activator traps in the cathode region. Because of the electrons trapped in this region, the internal field increasingly counteracts the external field. Thus, the luminescence decreases appreciably within an hour or so. Upon field reversal, the barrier in this region (now anode) has disappeared. Thus, it is only within the very first moment that a flash can appear. This results from the strong field between the metal anode and the semi-

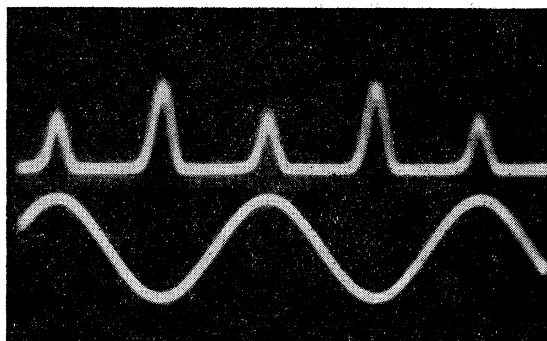


FIG. 4. Oscilloscope of photomultiplier current (upper curve) synchronized with the voltage across the crystal layer (60 cps; lower curve). The crystals are placed between insulating polystyrene foils.

conductor which had, in this region, sufficient trapped electrons from the start. Since upon reversal the field decreases instantaneously below the critical value, electron multiplication ends in this region. Once again, the field builds up at the other, second electrode, now cathode and barrier region, and the process is repeated. The ac polarization seems to be simply the result of established preferred and permanent barriers. This occurrence is such that, in some of the AlN crystals, the current is flowing from electrode 1 (anode, the barrier in the reverse direction being at electrode 2), while upon reversal the current in other crystals, with the barrier at electrode 1 (now the cathode), flows from electrode 2 (now the anode). The fact that with ac the luminescence glimmers and fluctuates until the barriers are formed in all crystals supports this concept. Ultraviolet has no effect since no light in the effective range  $<250 \text{ m}\mu$ <sup>11,16,17</sup> reached the material. The effect produced by infrared is not so clearly interpreted since it seems to break down the barriers, and the effect is annihilated after changing the contact points by moving the AlN crystals within the electrodes.

#### ACKNOWLEDGMENTS

The authors wish to express their appreciation to Dr. F. E. Williams, Dr. F. J. Studer, and Dr. S. Roberts from General Electric Company, Schenectady, New York, for the efficiency and absorption measurements and for helpful discussions; to Dr. J. A. Kohn for x-ray analysis; to R. O. Savage for spectrochemical analysis; and to C. Stochl for his invaluable help in the construction of various devices.

<sup>16</sup> E. Kauer and A. Rabenau, *Z. Naturforsch* **12a**, 942 (1957).

<sup>17</sup> Measurements by F. E. Williams *et al.*, indicate an absorption edge in the  $220 \text{ m}\mu$  spectral region.

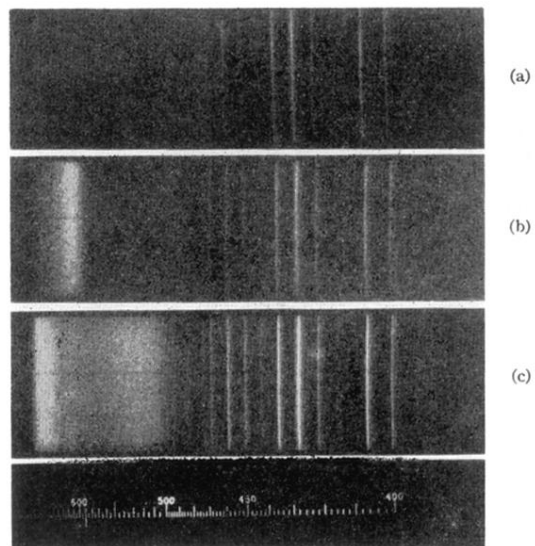


FIG. 1. Electroluminescent spectra emitted from AlN. (a) This spectrum is emitted from 99.99% pure sample. In the 400–500  $m\mu$  region is the narrow band structure of the second positive system of  $N_2$ , and in the 650–700  $m\mu$  region is a broad band. This spectrum is common to all other spectra regardless of the activator. The electroluminescence is blue in appearance. (b) This spectrum is emitted from sample with trace of Mn (0.001%). A broad band is seen in the 600–630  $m\mu$  region in addition to spectrum A. The electroluminescence is red in appearance. (c) This spectrum is emitted from sample activated with a high concentration of Mn ( $\sim 1\%$ ). Broad bands appear between 500 and 700  $m\mu$ . Note fine structure in the 650–700  $m\mu$  region. The electroluminescence is green in appearance.

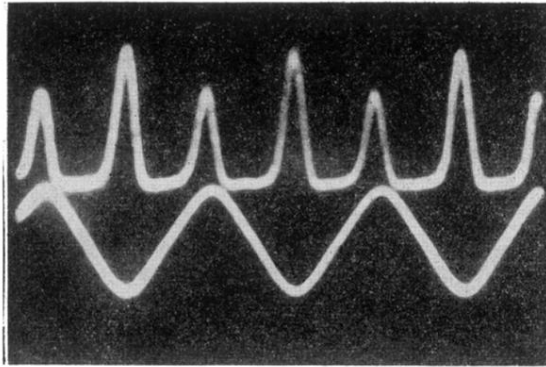


FIG. 3. Oscillogram of electroluminescence intensity (upper curve) synchronized with the current through the crystal layer (60 cps; lower curve). The current is nonsinusoidal due to the nonohmic characteristic of the crystals. The more intense light is emitted from the electrode 1 which is next to the multiplier.

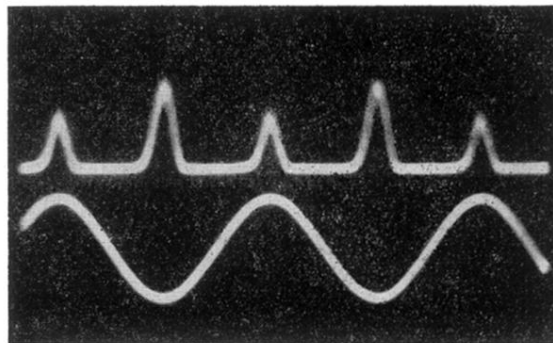


FIG. 4. Oscillogram of photomultiplier current (upper curve) synchronized with the voltage across the crystal layer (60 cps; lower curve). The crystals are placed between insulating polystyrene foils.