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Blue Anti-Stokes Electroluminescence in GaN

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Blue electroluminescence has been observed in GaN when the energy supplied to each electron is more than $48kT$ below the energy of the emitted photons. The emission increases with the cube of the current. An external power efficiency of 3×10^{-4} was obtained. Several excitation mechanisms by two hot electrons are considered.

Blue electroluminescence has been observed in GaN with an applied potential drop lower than the energy of the emitted photons. This observation contrasts with previous results obtained with GaN diodes in which the applied potential was at least four times larger than the emitted energy.[1] In the earlier experiments with metal–insulator–n-type structures, blue emission was obtained only when the metal was biased negatively with respect to the GaN; in the present work, the low-voltage blue luminescence occurs only when the metal is biased positively. Anti-Stokes electroluminescence has been seen in other materials such as GaAs[2,3] and ZnS.[4] In the work of Dousmanis et al.[2] the extra energy was believed to come from phonons (a refrigeration process). In the study of Nathan et al.,[3] higher energy initial states were populated by Auger recombination in a nearby region. Bitter, Indradev, and Williams[4] proposed that a hot electron from one region of ZnS produced a low-efficiency ($< 10^{-8}$) tunneling-assisted impact excitation in a second region of the crystal. Here I have evidence for a new and different type of mechanism. This new effect was observed in several crystals grown in two different reactors on different days.

The present structure was made by the chemical vapor deposition of GaN on sapphire.[5] First an undoped n-type conducting layer was grown; then a Zn-doped layer was grown, while the partial pressure of Zn was adjusted to barely compensate the native donors (nitrogen vacancies). For reasons not completely understood, in a constant ambient Zn concentration, the concentration of Zn incorporated in the crystal appears to increase gradually during growth.[6] Therefore full compensation occurs near the middle of the Zn-doped layer, where the resistivity of the material increases suddenly by several orders of magnitude. A large-area Ohmic connection is soldered to the edge of the n-type layer while a point contact rests on the semi-insulating layer.
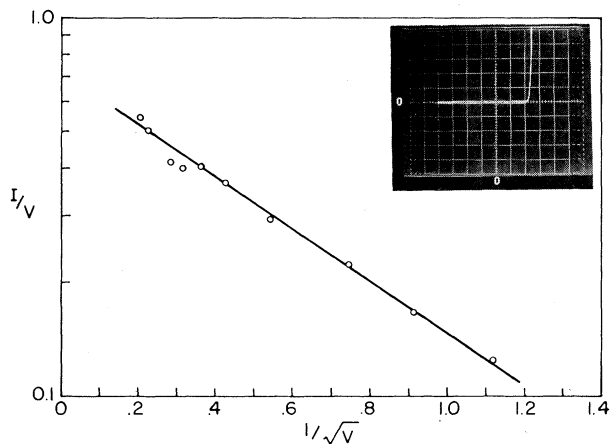
FIG. 1. Fowler-Nordheim plot of forward-bias characteristic (point contact positive). The $I(V)$ characteristics is shown in the inset; scale 1 μA per vertical division, 1 V per horizontal division.

FIG. 2. Emission spectra at 300°K (bias: 2.58 V, 4.8 mA) and 78°K (bias 2.4 V, 10 mA) obtained at two different points on same crystal.

As shown in Fig. 1, this structure has a rectifying $I(V)$ characteristic which, in the forward bias, obeys the Fowler-Nordheim relation,[7] namely, the logarithm of the conductance is inversely proportional to $1/\sqrt{V}$. This behavior suggests that charge transport is a tunneling process.

Blue light is visible under the point contact when the dc bias exceeds 2.1 V. Figure 2 shows the emission spectra obtained at 300 and 78°K. The emission peaks at 2.9 eV and does not shift with the applied bias. The blue spectrum at 2.9 eV was intense enough to be recorded even with a 2.2-V bias. The light intensity increases with the third power of the current, as shown in Fig. 3. This cubic dependence is a new observation and is crucial to the interpretation of the mechanism. An external power efficiency of 3×10^{-4} and a quantum efficiency of 2×10^{-4} were obtained at room temperature. This is the highest efficiency reported for blue dc electroluminescence.

With a point contact, the anti-Stokes emission is obtained at a current density of the order of 10^3 to 10^4 A/cm^2. When a larger area In dot is used instead of a point contact, pulsed excitation must be used to avoid melting the In electrodes. Under pulsed excitation, blue light was obtained at a voltage as low as 1.64 V. This represents a potential difference almost a factor of 2 lower than the energy of the emitted photons—an energy discrepancy of $48kT$. (The discrepancy is even greater at low temperature.) The pulsed-light intensity still increased with the cube of
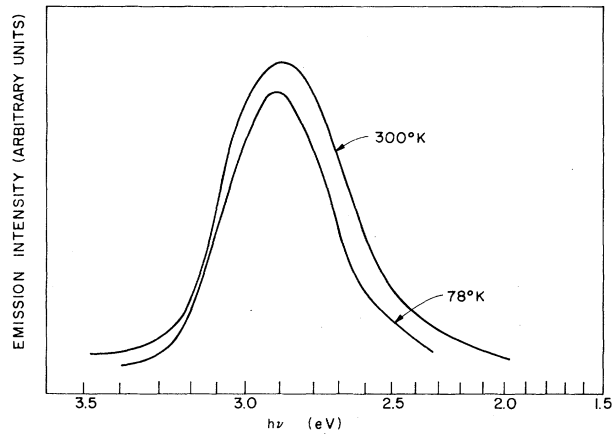
the current.

A tentative interpretation of this phenomenon is predicated on the occurrence of a high electric field localized at the insulator–n-type (i-n) transition in the structure. An analysis of the earlier form of GaN light-emitting diodes showed that the luminescence results from impact excitation at the cathode interface of the i layer.[8] In the present case, the n layer is the cathode. Observations under a microscope with a point contacting the fractured edge of the i layer confirmed that light is emitted 10 μm below the surface inside the 40-μm-thick Zn-doped layer, presumably at the i-n interface (recall that part of the Zn-doped layer is undercompensated and therefore still n-type conducting).

A tentative band diagram of the present arrangement in the presence of an applied forward bias is sketched in Fig. 4. The barrier at the i-n transition inside the Zn-doped layer could be due to a local increase in Zn concentration. This barrier is needed to explain the $I(V)$ characteristic and to localize the high electric field. Electrons which tunnel through the barrier at the n-i transition become hot electrons which can lose their energy by colliding with a Zn center. Blue luminescence requires than an electron be excited out of the Zn center. For our range of voltages, this process could result from the simultaneous collision of two hot electrons with the Zn center. Alternatively, an electron can be double-impact excited from the valence band across the energy gap whereupon the Zn center traps the resulting hole. A further possibility is a two-step excitation out of either the Zn center or the va-
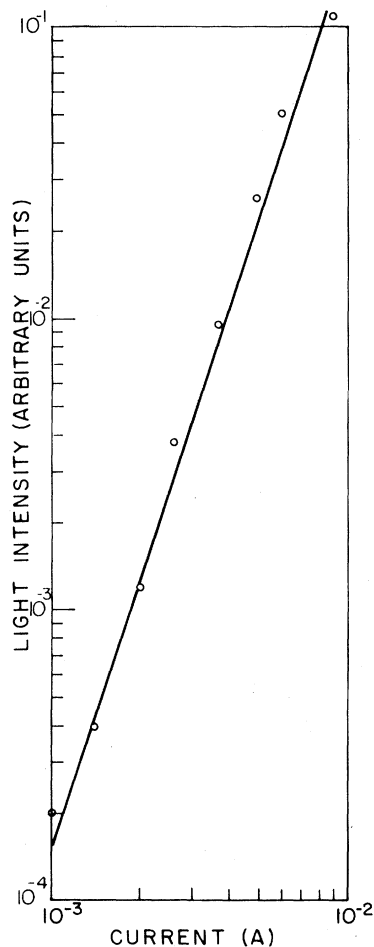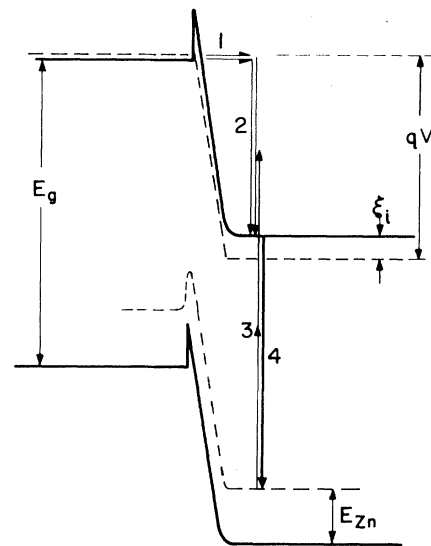
FIG. 3. Emission intensity versus dc current.

FIG. 4. Band diagram and proposed model for the anti-Stokes process: (1) tunneling of two electrons, (2–3) energy exchange between the two hot electrons and an electron trapped at Zn center, (4) radiative recombination at impact-excited Zn center.

lence band via some intermediate state reached by a first impact and from which the electron is subsequently excited by a second impact.

In either of these excitation processes, the number of empty final states for the radiative transition to the Zn center should increase quadratically with the current, I. Since the number of final states increases as I^2 and the number of electrons in the initial radiation state (assumed to be the conduction band) increases as I, the intensity of the emitted light should increase as I^3, as observed (Fig. 3).

Although the simultaneous impact excitation by two hot electrons would be expected to have a low probability, this low probability is offset by the ease of satisfying energy and momentum conservation, especially for the excitation of a deep center. This is consistent with the observed efficiency of 3×10^{-4}. In contrast, the one-electron process with a $48kT$ energy deficiency would

have the negligible excitation efficiency of $\sim 10^{-21}$.

The lowest threshold voltage, V, for the onset of the anti-Stokes process is given by

$$qV = (E_g - E_{Zn})/n + \xi_i,$$

where n is the number of hot electrons participating in the simultaneous collision of the Zn center and the other symbols are identified in Fig. 4. In the present case $E_g - E_{Zn} = 2.9$ eV, $n = 2$; the observed threshold voltage of 1.65 V would require that the Fermi level be 0.2 eV below the conduction band at the surface.

Although higher-order processes than those involving two hot electrons are conceivable, their probability should be extremely low. The direct impact excitation by a single hot electron ($n = 1$) is not observed in the present material because it would occur at current densities beyond those resulting in catastrophic degradation.

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Exact-Exchange Crystal Hartree-Fock Calculations of Molecular and Metallic Hydrogen and Their Transitions*

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Hartree-Fock calculations using the exact-exchange operator are reported for molecular and metallic solid hydrogen. Both calculations used the same basis set and the same crystal formalism. The calculations indicate a transition to the metallic phase at a pressure of 2.1 Mbar, in agreement with recent experiments.

In recent years there has been a widespread interest in the possibility of producing metallic hydrogen in the laboratory[1] by means of a pressure-induced transition from the molecular phase. To determine the feasibility of such a process, it is important to have some estimate as to the pressure needed. Previous calculations[2-5] have produced estimates ranging from 0.25 to 20 Mbar, the lower pressure being relatively easy to reach in the laboratory, and the higher pressure out of reach at least statically.[6] Recent experimenters[7-8] achieving high pressures dynamically suggest that they may have detected the transition at pressures of 2.0 to 2.8 Mbar. In this Letter we present preliminary results which are obtained from calculations more rigorous than those previously performed, and which support the experimental evidence of a possible transition.

Theoretical estimates of the pressure required for the transition at zero temperature are obtained from the common tangent to the energy-volume curves for the two solid phases. Most of the previous estimates have been based on fairly similar equations of state for the metallic phase, but have used widely different and less reliable equations of state for the molecular phase. In fact, the metallic-phase equation of state recently obtained by Neece, Rogers, and Hoover[2] from the self-consistent calculation, using the Kohn-Sham local potential to approximate exchange and correlation effects, is not substantially different from the approximate cellular calculation by Wigner and Huntington[3] in 1935. The molecular-phase equation of state has been obtained by solving the Bethe-Goldstone equations using an approximate analytically fitted curve for the H_2-H_2 interaction potential.[5] Forms such as the Lennard-Jones 6-12 or 6-8 potentials were used, with parameters obtained either from experimental virial coefficients and viscosities for molecular hydrogen, or from variational calculations of the interaction of two H_2 molecules.[9] The molecular-phase equation of state varies sharply with the choice of parameters, with the result that estimates of the transition pressure based on slightly different H_2-H_2 pair potentials vary from 0.84 to 4.2 Mbar.[10] A main difficulty with all the previous work is that the metallic and molecular crystals are not treated in an internally consistent degree of approximation.

The calculations presented here are based on the techniques developed by Harris and Monkhorst[11] for the computation of Hartree-Fock wave functions and energies. In their method each valence Bloch orbital $|\vec{k}\rangle$ is expanded according to

$$|\vec{k}\rangle = \sum_m C_m(\vec{k})|k_m\rangle, \tag{1}$$

where the $|\vec{k}_m\rangle$ are basis Bloch functions with Bloch wave vector $\vec{k}$:

$$|\vec{k}_m\rangle = \exp(i\vec{k}\cdot\vec{r})\sum_\mu \sum_{n=1}^d \varphi_m(\vec{r} - \vec{R}_\mu - \vec{s}_n). \tag{2}$$

The sum over μ in Eq. (2) runs over all the lattice cells, $\vec{R}_\mu$ is the origin of cell μ, and $\vec{s}_n$ is the position relative to the cell origin of atom n. The φ_m are Slater-type atomic orbitals, and the
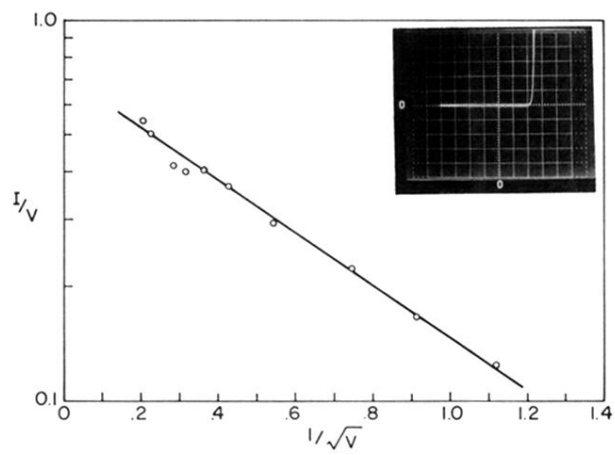
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