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DONOR-ACCEPTOR PAIR RECOMBINATION IN GaN

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Photoluminescence arising from distant donor–acceptor pair recombination in GaN has been identified and analyzed. Impurity binding energies of $E_D = 42 \pm 1$ meV and $E_A \sim 200$ meV are proposed. The recombination rate constant, $W(O) = (3 \pm 2) \times 10^7$ sec^{-1} is consistent with a direct, fundamental energy gap in GaN.

LUMINESCENCE from the hexagonal III–V semiconductor gallium nitride is not well understood. A few early reports (1958–1962) outlining the general features of the photoluminescence (*PL*) have appeared.[1–3] Very recently, several further articles [4–8] have been published. No detailed mechanisms have been identified, although Grimmeiss and Monemar[8] have suggested that donor-acceptor pair recombination might be responsible for the 3.3–3.0 eV emission from powder samples. The recent availability of single crystals of GaN, either as free hexagonal rods and platelets [9] or as epitaxial layers [10] has stimulated a reappraisal of the technological potential of this material. From this standpoint, it is essential that a better understanding of the luminescence from GaN be achieved.

In this communication we report the first detailed analysis of the low-temperature luminescence from single crystal GaN. Here we are mainly concerned with a characteristic series of bands that appears in the range 3.26–2.99 eV in spectra taken from vapor-grown epitaxial layers and free single-crystal hexagonal needles. The results of the investigation demonstrate that these bands arise from zero-phonon transitions and LO–phonon replicas associated with distant donor-acceptor pair recombination. From an analysis of the data, donor and acceptor binding energies and a recombination rate constant, $W(O)$ are obtained.

EXPERIMENTAL

Undoped single crystalline GaN was grown epitaxially from the vapor phase on <0001> oriented sapphire substrates. The growth procedure closely follows a previously described technique [10] and uses NH_3 as the source of nitrogen while Ga is transported as its subchloride by reaction with HC1 gas. Substrate temperatures were in the range 1040–1060°C. The appearance of the deposited layers varies from colorless to grey depending on the distance of the substrates from the gas reaction zone. The growth apparatus is all quartz with the exception of an Al_2O_3 boat which contains the Ga melt. Helium, purified by passage through a liquid nitrogen trap, is used as the carrier gas. Care was taken to reduce inadvertent impurity contamination by using electronic grade Ga, 99.999 per cent pure NH_3 and 99.99 per cent HCl as reagents. Electrical measurements indicate $n \sim 10^{18}$–$10^{19}/cm^3$ in most of our undoped layers. Judging from the optical results, the crystals are somewhat inhomogeneous with small areas that appear to be considerably less heavily doped than $10^{18}/cm^3$. It is on these areas that the present opical experiments have been conducted.

Luminescence was excited with a pulsed nitrogen gas laser ($h\nu = 3.68$ eV). Absorbtion

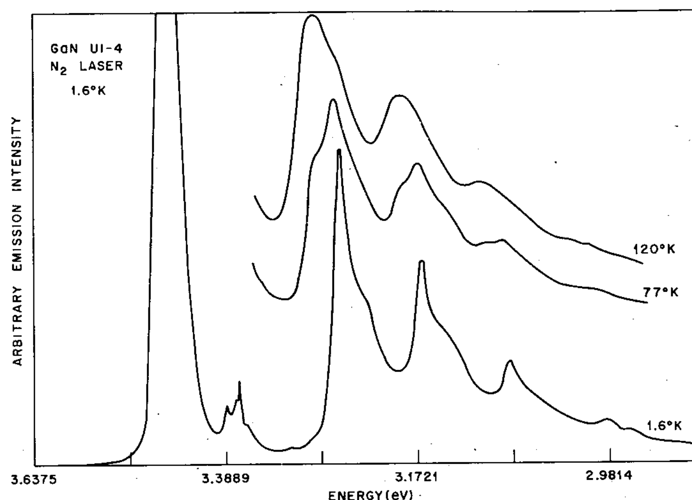

FIG. 1. Typical photoluminescence from epitaxial layers of GaN. In this Communication, the features below 3.30 eV are discussed. The temperature dependence of the shape of the 3.26 eV band between 1.6° and 120°K is clearly shown.

measurements[6,10] indicate that $\alpha \gtrsim 2 \times 10^5\ cm^{-1}$ in this region. Appropriate experiments show that crystal heating by the exciting beam is not a significant factor in this study. Temperatures other than those in the liquid helium range were attained and monitored in the manner described earlier.[11] Radiative lifetimes and time-resolved spectra were obtained in a similar way.[11] In the present case, however, a cooled EMI 9558Q photomultiplier was used and the time resolution of the apparatus was about 20 nsec. For the experiments to be described this decay time is negligibly short.

RESULTS

Figure 1 shows the near u.v. emission from a 250 μ thick epitaxial layer. This spectrum is typical of that seen in a number of colorless epitaxial layers and free single crystal needles. Although the features at $\gtrsim$ 3.37 eV are of considerable interest,[12] in this Communication we shall confine ourselves to the series of bands that extends from 3.257 eV into the violet region of the visible spectrum.

At 1.6°K these bands have a characteristic shape, the origin of which will be discussed below. Initially, however, it is important to demonstrate that the regular spacing of 90 ± 1 meV between the bands at 3.2571, 3.1672 and 3.0768 eV is due to the coupling of phonons to the transition at 3.2571 eV. Apart from the regularity of the spacing and the conservation of the peculiar band shape, which are quite suggestive, we have measured the radiative lifetimes of the first three members of the series and we find that they are identical. Moreover, all other emissions from the crystal have lifetimes that are orders of magnitude faster and they obey a different type of decay kinetics. These experiments firmly establish the vibronic nature of the 3.1672 and 3.0768 eV bands. We assign the vibrational frequency to the 'unperturbed' [13] zone-center longitudinal optical phonon. This value for the LO is in good agreement with the estimates made recently by Manchon *et al.*[13] from i.r. data. Furthermore, this phonon spacing occurs in spectra from free single crystal needles (as used by Manchon *et al.*) as well as from other epitaxial layers, and there is little doubt that it is characteristic of the GaN lattice.

As the temperature is raised, the rather steep high energy edge of each feature (low excitation intensity) is broadened, and at ~ 30°K a new, high-energy band (HEB) appears. By ~ 120°K this new HEB completely dominates this region

of the spectrum (Fig. 1). At intermediate temperatures there is absolutely no doubt that two bands exist simultaneously. The separation of these bands in 30 $\pm$ 5 meV in good accord with the thermal activation energy of 30 $\pm$ 10 meV that we obtain for the quenching of the lower-energy band (LEB). The large error in this latter energy is due to the difficulties involved in resolving the two overlapping bands at intermediate temperatures.

This type of temperature dependence is reminiscent of that found in CdS and ZnSe, where similar spectra have been associated with distant donor-acceptor pair recombination (LEB) and free electron-bound hole transitions (HEB).[14, 15] A characteristic shift and broadening of LEB to higher energies is expected if the excitation intensity or the temperature is increased. We have observed such effects in our GaN spectra (see Fig. 1 for temperature effects).

A definitive test of the DA pair recombination mechanism is the behavior of radiative lifetimes and time-resolved spectra (TRS). The first should be nonexponential, whereas the latter should show a shift to lower energies and a narrowing as the time delay after the pulse excitation is lengthened. The lifetimes measured for the first three members of the series (at 1.6°K) are identical. The non-exponential nature of the decay is shown in Fig. 2. Also shown are decay rates for other regions of the spectrum. These are very fast and essentially exponential. In crystals of poorer quality (as judged by linewidth, resolution, etc.) the 3.26 eV band can also decay in a fast, essentially exponential manner. Apparently the impurity concentration of these crystals ($n \gtrsim 10^{19}/\text{cm}^3$) precludes the application of the classical, distant DA pair model.[16]

TRS completely confirm the DA hypothesis for the 3.26 eV system. As shown in Fig. 3 the spectra narrow and shift to lower energies as the time delay after the pulse is increased. At long times, there is some indication that the unusual shape of the individual bands arises not from low energy phonon cooperation, but from the near superposition of two DA systems. If this is the case, the decay kinetics of the two systems must be very similar.[17]

The evidence presented above leaves little doubt that this spectrum arises from DA recombination. In this case, the results may be analyzed to give values of E_D, E_A, E_C (the Coulomb energy of the DA pair at any instant in time), and $W(O)$, a recombination rate constant[16] that should be characteristic of GaN.

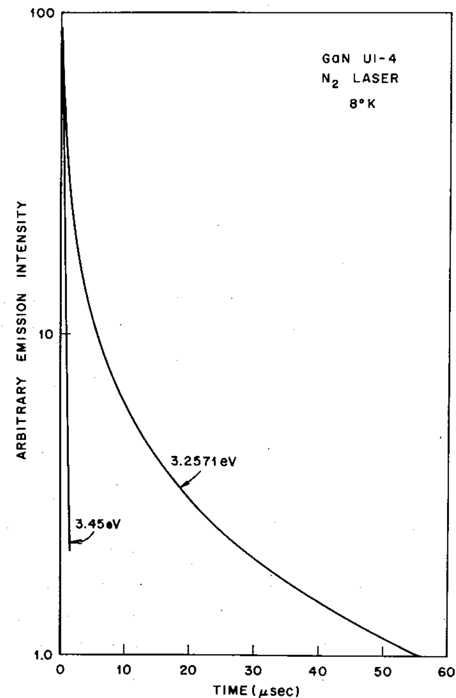

FIG. 2. Radiative lifetimes of the 3.2571 eV and the 3.45 eV emission bands at low temperatures. The results for the 3.45 eV band are limited by the time constant of the apparatus.

Direct-gap semiconductors (III–V and II–VI, Zinc blend and Wurtzite) with the lowest conduction band minimum at $\Gamma(k = o)$ invariably have $m_e^* < m_h^*$. This relationship imposes the restriction that effective-mass donors be more shallow than effective-mass acceptors. Mainly because of this general relationship between m_e^* and m_h^*, we choose the donor to be the more shallow impurity involved in these DA spectra. Thus we begin by associating the 30 $\pm$ 5 meV separation between LEB and HEB with E_D. In actual fact, the value of E_D used is 42 meV; a choice which we justify below. With this value, which we assume to be the effective mass binding energy, and $\epsilon_0 = 9.8$[13] one derives $m_e^* = 0.25\,m$.

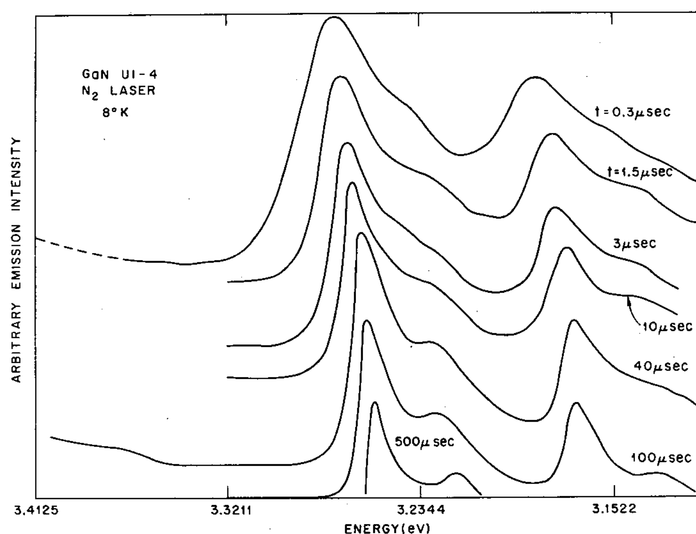

FIG. 3. Time-resolved spectra from GaN at low temperatures. The shift and narrowing of the 3.26 eV band as the time delay after the pulse is increased is clearly shown. The 500 μ sec spectra appear to show this band resolved into two, a behavior which is not consistent with the hypothesis that the band shape is produced by coupling to low-energy phonons.

Using this value of m_e^*, ϵ_0 = 9.8, and m_h^* in the range 1 to 2, the free exciton binding energy lies in the range 28 meV (m_h^* = 1) to 31 meV (m_h^* = 2). The well-defined structure at 3.470 ± 0.008 eV in the absorption and reflectance spectra[6] of the epitaxial layers used in the present investigation may correlate with the onset of intrinsic absorption. For the purpose of the following discussion, we tentatively assign the 1.6°K energy gap of these epitaxial GaN layers as 3.500 ± 0.010 eV.

The HEB (3.287 ± 0.002 eV) is attributed to a free electron-bound hole recombination. The acceptor binding energy, $E_A = E_g$ − HEB is thus 213 ± 12 meV. Combining this value with the chosen E_D shows that when E_c = 0 (i.e. when r, the donor-acceptor pair separation approaches ∞), a narrow emission line should appear at 3.245 eV. From the TRS, the value of E_c for the particular set of pairs decaying at any given time can now be evaluated. For example at 100 μ sec delay, E_c = 13 ± 4 meV. At this time the decaying pairs are about 120 Å apart. The TRS have been, analyzed using values of E_C, E_D and E_A that are in reasonable accord with those derived above. We find that the best value of $W(O)$ is (3 ± 2) × 10^7 sec^{-1}. For this result, E_D = 42 meV, and E_C = 19.6 meV at 100 μ sec delay. The need to increase the value of E_D over the 'apparent' value obtained from the separation of HEB and LEB probably arises from the fact that E_g is not known accurately, neither at 1.6°K (where LEB dominates) nor in the range of 100°K where HEB dominates. The value derived from the spectra (with no correction for the temperature dependence of E_g nor any correction for E_C), should be regarded as a lower bound for E_D.[18]

CONCLUSIONS

In the initial evaluation of a new material, or as in the present case, for a reevaluation of a material that has been known for some time, it is important to demonstrate mechanisms, assign parameters and provide round figure estimates of important quantities. More refined results must, of course, follow, but only at a time when the models are thouroughly tested and the details fully understood.

In this paper we have demonstrated the existence of distant DA recombination processes in GaN. Moreover, it is clear that this mechanism is responsible for a sizable part of the near u.v. emission at low temperatures. From an analysis of the decay kinetics and thermal quenching processes (to 150°K) binding energies of the participating donors and acceptors have been

derived. Finally, the recombination rate constant, $W(O) = (3 \pm 2) \times 10^7$ sec^{-1} is quite consistent with, and provides very strong support for the suggestion[6] that GaN is a direct gap semiconductor.[18] Other experiments, concerned with this point, with the chemical nature of donors and acceptors, and with the other features in the luminescence will be reported in due course.

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13. See MANCHON D.A., Jr., BARKER A.S., Jr., DEAN P.J. and ZETTERSTROM R.B., *Solid State Commun* **8**, 1227 (1970). In the present paper we use $\omega_{LO} = 9$ meV, $\omega_{TO} = 69$ meV, and the Lyddane–Sachs–Teller relationship to derive $\epsilon_0 = 9.8$.
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17. If there are two or more separate DA spectra under the band envelope it is unlikely that both systems would exhibit *identical* decay kinetics. In particular, this near superposition would interfere with the detailed analysis of the TRS from which the rate constant $W(O)$ is evaluated. Although we do not intend to discuss the details here, we have experienced some difficulty in obtaining consistent values of $W(O)$, especially from TRS taken close to the exciting pulse. It is just this region of time that we expect to be most strongly affected by overlapping DA spectra. The values of $W(O)$ to be given here are based upon TRS obtained further from the exciting pulse.
18. Screening effects, arising from the relatively high donor concentration in these crystals, will also affect these results (see for instance BONCH-BRUEVICH V.L. in *Semimetals and Semiconductors*, Vol. 1, p. 106, (edited by WILLARDSON R.K. and BEER A.C.) Academic Press, New York, (1966). In particular, TRS at short times may not be consistent with results obtained at longer delay times (see reference 17), because for these fast decaying pairs screening effects will be enhanced, especially if the diping is somewhat inhomogeneous.
19. Similar experiments of *direct* gap materials give $W(O) = 4 \times 10^8$ sec^{-1} (CdS), $(3 \pm 2) \times 10^8$ sec^{-1} (GaAs) and 6.5×10^7 sec^{-1} (InP). (Indirect GaP has $W(O) \approx 5 \times 10^5$ sec^{-1}.

La photoluminescence provenant de recombinaisons entre paires distnates du type donneur-accepteur a été identifiée et analysée dans le nitrure de gallium. Des énergies de liaison d'impuretés $E_D = 42 \pm 1$ meV et $E_A = 200$ meV sont proposées. La valeur du taux de recombinaison $W(O) = (3 \pm 2) \times 10^7$ sec^{-1} est en accord avec l'existence d'une bande fondamentale directe dans le GaN.