

Time-resolved luminescence studies of heavily nitrogen doped ZnSe

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Time-resolved luminescence data from heavily nitrogen doped ZnSe (total N concentration exceeding mid- $10^{18}/\text{cm}^3$) is presented. The luminescence exhibited a decay time and a rise time which increased with decreasing energy of observation. Furthermore, both the decay times and rise times decreased with increasing temperature. These observations are consistent with the following model: (i) a band of states is created due to fluctuations in the ionized impurity concentrations; (ii) a portion of the carriers captured by the shallower impurity states are transferred to deeper states prior to recombination. © 1996 American Institute of Physics. [S0003-6951(96)00637-7]

Currently, nitrogen doping appears to be the only feasible way of achieving good *p*-type conductivity in ZnSe, which is especially useful in II–VI based visible light emitting devices. Although current levels of doping are sufficient for the demonstration of a II–VI laser operating in the blue-green region of the spectrum, further improvements in device performance are expected with increasing conductivity.¹ With increasing nitrogen concentrations ([N] above $10^{17}/\text{cm}^3$), the doping efficiency is reduced due to the increased creation of compensating donor species, possible due to complexes formed by nitrogen with selenium vacancies (V_{Se}).² These donors can be identified in the photoluminescence (PL) spectra, specifically in the donor–acceptor pair (DAP) region, as a second, deeper, series of peaks in addition to the series corresponding to a shallow donor.² When the nitrogen concentration gets into the $10^{18}/\text{cm}^3$ range, the PL shows a deep broad band whose peak ranges between 2.5 and 2.65 eV.^{3,4} Previous PL studies^{5,6} show that this peak is due to a “modified DAP luminescence,” where the fluctuations in the ionized impurity concentrations give potential fluctuations, leading to a broad band of states. In this letter, we present time-resolved luminescence (TRPL) data from these “modified DAP” bands, and propose a mechanism to explain the observations.

The ZnSe:N sample used in this study was grown on a GaAs substrate by MBE.⁷ The free hole concentration was $2.6 \times 10^{17}/\text{cm}^3$, and the total nitrogen concentration was estimated to be between mid- $10^{18}/\text{cm}^3$ and low- $10^{19}/\text{cm}^3$. The time-resolved luminescence data were collected using a pulsed nitrogen laser operating at 337 nm, with a pulse width of about 3 ns. The luminescence was collected, and focused on a 3/4 m monochromator which was coupled to a fast photomultiplier tube. The system was capable of a resolution of roughly 5 ns. The sample temperature was accurately controlled and monitored using a silicon diode mounted in close thermal contact to the sample.

Figure 1 shows the TRPL at different wavelengths. The inset shows the PL from the same sample. TRPL from energies lower than 2.637 eV contained significant contributions

from the phonon replica of the main peak (shown in the inset). Although the TRPL data could not be adequately described by simple exponential functions, it shows a characteristic luminescence decay time,⁸ which increases with decreasing energy. The data also show a rise time which increases with decreasing energy; rise times were not observed in low-doped samples in our TRPL system. The temperature dependence of the TRPL is shown in Fig. 2. It can be seen that, in addition to the quenching of the PL intensity⁵ with increasing temperature, there is a decrease in both the rise time and decay time.

TRPL from DAPs has been studied in several semiconductors.^{9–11} The standard model⁹ assumes that the rise time is significantly faster than the decay time of luminescence. However, as shown in Fig. 1, in the heavily doped case this is not so. Furthermore, the observed phenomena are different from those reported for ZnSe:Na¹² (the TRPL from

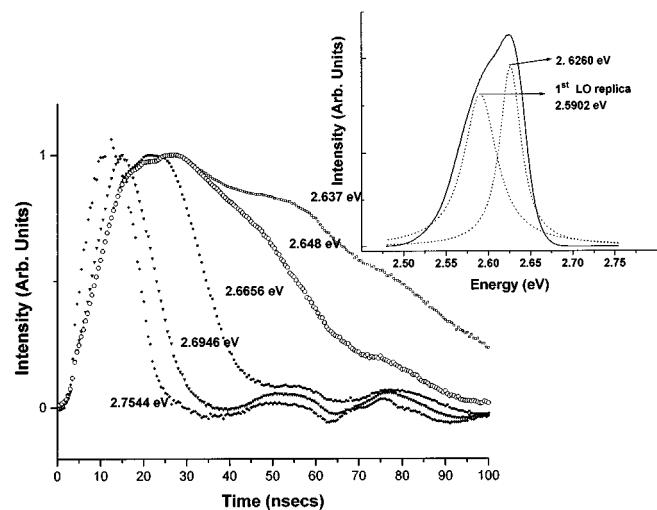


FIG. 1. The TRPL is shown for some representative wavelengths; the intensities were normalized to their peak positions. The bumps in the intensity occurring around 60 ns were caused by the inherent response of the photomultiplier tube. The inset shows the PL from the sample; the dotted curves were obtained by the best fit of two Gaussians to the original data shown as a solid line. The difference in peak positions is, within the order of the numerical error (5 meV) of fitting, the value expected in ZnSe for phonon replicas.

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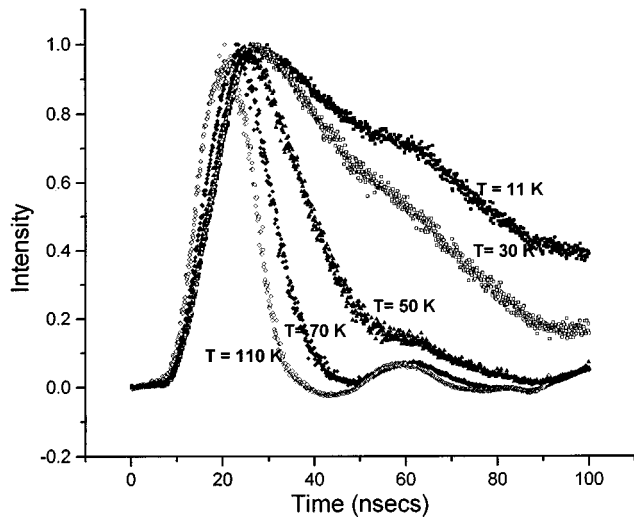


FIG. 2. The temperature dependence of the TRPL is shown for some representative temperatures. Both the rise times and decay times decreased with increasing temperatures.

ZnSe:Na is expected to behave similarly to the TRPL in low doped ZnSe:N, owing to their similar energies). A model that is consistent with our present time-domain observations as well as previously reported steady-state PL data from heavily doped ZnSe:N,^{5,6} is shown schematically in Fig. 3. Here, the fluctuations in the ionized impurity concentration lead to a distribution of spatially separated potential wells in both the impurity and band states [alternative models such as impurity banding, where the presence of other donors perturb the donor level, are not likely to be significant at these impurity concentrations owing to the relatively deep (~ 45 meV), compensating, donor; furthermore, the line shape expected from impurity banding,¹³ a sharp, high energy edge followed by a low energy tail, is not observed in the PL^{5,6}]. A carrier that is captured at an impurity site, in addition to direct recombination with a carrier of the opposite type, can transfer to a state lower in energy prior to recombination, giving rise to a lower energy photon. This leads to the PL band given as¹⁴

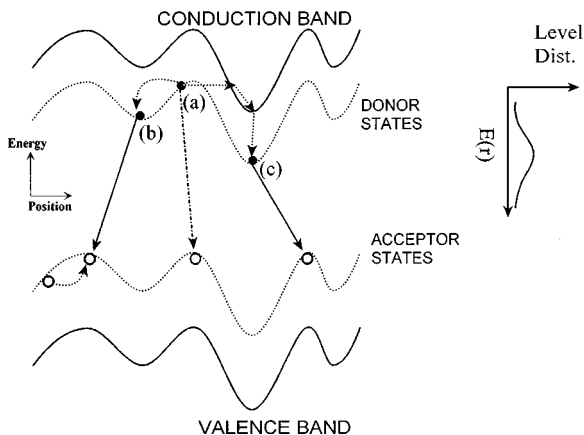


FIG. 3. Schematic representation of the recombination process in the presence of fluctuations. An electron captured at a donor site (a), in addition to the probability for direct recombination, has a probability to transfer to states lower in energy (b) and (c), thus leading to a lower energy emission. This also decreases the decay time of emission (a).

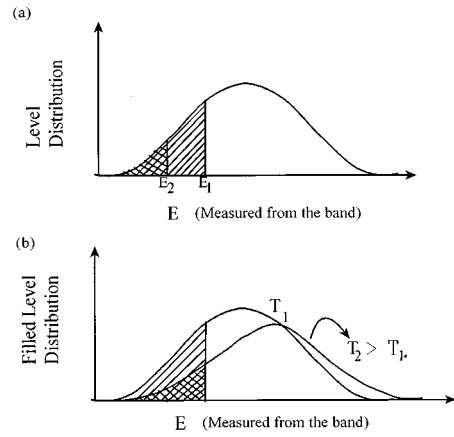


FIG. 4. A representation of the distribution of levels: (a) the shaded areas represent the number of states within an energy E_1 or E_2 from the band; with increasing energy of emission (smaller E from the band) there is a smaller number of levels above that energy (b) shows the distribution of filled levels (i.e., those which can emit photons) with increasing temperature (from PL it is known that the filled level distribution widens and shifts to the red, in addition to the decrease in total intensity); at higher T , there is a smaller number of filled states above a given energy; see discussion for the effect on the observed decay time and rise time.

$$E(\hbar\omega) \cong E_G - (E_D + E_A) - 2\sigma, \quad (1)$$

where σ is the half-width of the fluctuations and the rest of the notation is standard.

The observed decay time,⁸ t_d , at a given energy, is composed of both the radiative lifetime (t_r) and the contribution due to the transfer processes (t_{tr}), which deplete the population without contributing to the intensity at the energy of observation, and can be written as

$$1/t_d = 1/t_r + 1/t_{tr}. \quad (2)$$

Similarly the rise time would contain contributions from both the capture time and contributions due to the incoming transfer processes.

With increasing energy of observation, the photons come from carriers captured at shallower states, and these carriers find a larger number of states lower in energy to transfer to [Fig. 4(a)], and hence decrease the decay time via (2).¹⁵ The rise time of the luminescence similarly decreases with increasing energy of observation, due to the decreased incoming transfer from shallower levels (there are not as many states that are shallower to transfer from, and hence there is mainly direct capture from the band, which is assumed to be fast). With increasing temperature, the thermalization from the levels increases; thus, at a given energy of observation, as the temperature is increased, the addition of thermalization to the recombination decreases the decay time via (2). Moreover, thermalization preferentially depopulates the shallower states. Thus, at a given energy of observation, as the temperature is increased, the number of filled states above that energy is decreased [Fig. 4(b)]. This leads to a decrease in the influx of carriers into the state, resulting in a decreased rise time.

Although these TRPL results are indicative of transfer among localized states, there could be more than one pathway for the transfer (Fig. 3); a more detailed analysis, which takes into account various transfer processes, is needed to

quantitatively fit the TRPL data. Furthermore, these results confirm the presence of fluctuations in heavily N-doped ZnSe, and point to their role in the luminescence. The existence of these fluctuations suggests an inhomogeneity in the material; it is known that inhomogeneities can result in persistent photoconductivity (PPC).¹⁶ Based on these results, it is expected that heavily doped ZnSe:N would exhibit such persistent behavior. It has been shown previously that PPC could be used for data storage,¹⁷ and for other novel optoelectronic applications.¹⁸ It is possible that heavily doped ZnSe:N could play a useful role in these emerging applications, and we plan future investigations on these topics.

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