Exciton tunneling inhibited by disorder in $GaAs_{1-x}P_x$:N

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A simple theory of exciton tunneling in $GaAs_{1-x}P_x$:N is presented. Excitons bound to nitrogen (N_x) tunnel to sites of lower energy within a disorder-broadened line. They continue to tunnel until there are no sites of lower energy within an effective tunneling radius. This radius grows slowly with time. The theory explains the absence of luminescence from NN pairs at low temperatures and the nonthermal N_x luminescence line shape. Monte Carlo simulations confirm the dynamics of the tunneling.

INTRODUCTION

In $GaAs_{1-x}P_x$:N, the energies of excitons bound to isolated nitrogen (N_x) are inhomogeneously broadened due to different As-P configurations around nitrogen atoms[1,2] (disorder broadening). Several authors[3,4] have observed that the steady-state (cw) N_x luminescence spectrum peaks at lower energy than the resonant excitation and absorption spectra. Recent time-resolved luminescence measurements[5] have demonstrated that this shift is due to exciton tunneling within the N_x band to sites of lower energy. In contrast to the alloy, the N_x band in GaP:N is very narrow, and no shift is observed between excitation and emission.[6] In heavily doped GaP:N ([N] $\gtrsim 5\times10^{17}$ cm^{-3}), however, excitons have been observed to tunnel[7] from the N_x traps to the deeper NN_i traps, where NN_i represents two nitrogen atoms which are ith nearest neighbors. Presumably excitons tunnel many times among the more numerous N_x sites before tunneling to an NN_i site, although one cannot observe the N_x intraband tunneling directly in GaP:N because the band is so narrow. The $N_x \rightarrow NN_i$ tunneling is so efficient in GaP:N that the NN_i pair levels dominate the luminescence[6] for [N] $\gtrsim 10^{18}$ cm^{-3}, even though there are 100 times as many N_x traps. In spite of the observed intraband N_x tunneling in $GaAs_{1-x}P_x$:N alloys and the $N_x \rightarrow NN_i$ tunneling observed in GaP:N NN_i, luminescence is never observed[8] in the alloy (regardless of N concentration) at temperatures below about 20 K. In this publication, a theory of exciton tunneling is proposed which explains the absence of NN_i luminescence in spite of the observed N_x intraband tunneling. The theory shows how the disorder broadening can inhibit the tunneling within the N_x band so that the excitons do not reach the NN_i traps, yet allows enough tunneling to account for the time-resolved luminescence spectra. Given the N_x density of states as measured by excitation, a quantitative prediction of the emission line shape is made which agrees with experiment.

THEORY

At large enough distances r from the nitrogen site, the bound exciton wave function decays exponentially with distance as e^{-r/a_0}, where a_0 is the effective exciton radius. The tunneling rate to another nitrogen site located a distance R from the first is $\Gamma_T(R)=\nu_0 e^{-2R/a_0}$. We take ν_0 constant for tunneling to sites of lower energy and zero for sites of higher energy, so that excitons tunnel only to sites of lower energy. Now, instead of thinking of a tunneling rate which falls exponentially with distance, we may think of a tunneling radius R_0 which grows logarithmically with time according to

$$R_0(t)=a_0\ln(\nu_0 t)/2 \ , \tag{1}$$

which is obtained by taking $\Gamma_T(R)=1/t$ above. The essence of the theory is that an exciton trapped at one N_x site will tunnel to any site of lower energy within R_0 in time t. Any site which has no lower-energy sites within R_0 will be called a local energy minimum site. Once an exciton is trapped on such a site, it remains there until it decays (mainly radiatively) or else R_0 increases to encompass an N_x site of still lower energy, in which case the exciton tunnels again. Under pulsed excitation, the time evolution of the distribution of local energy minimum sites describes the time evolution of the exciton population (and hence the luminescence). Under cw excitation, a mean value of the tunneling radius may be defined by $R_0(\tau)$, where τ is the exciton lifetime. The cw emission spectrum may be calculated from $R_0(\tau)$.

The distribution of these local energy minimum sites is straightforward to calculate. Let $n_0(E)$ be the density of exciton traps of energy E, normalized to unity. Suppose each site has, on average, m other N_x sites within R_0. The probability $P_m(E)$ that a site of energy E is a local minimum is the same as the probability that the other m sites are each of energy greater than E. The distribution of local energy minimum traps is therefore

$$n_m(E)=n_0(E)P_m(E)=n_0(E)\left[\int_E^\infty n_0(E')\,dE'\right]^m \ . \tag{2}$$

Equation (2) has been used previously[9] to describe the trapping of photoexcited carriers in amorphous silicon. In particular, for $n_0(E)$ a Gaussian centered on E_0 with standard deviation σ,

$$n_m(E)=\frac{1}{\sqrt{2\pi}\sigma}\exp\left[\frac{(E-E_0)^2}{2\sigma^2}\right]\left[\frac{1}{2}-\frac{1}{2}\,\mathrm{erf}\left[\frac{E-E_0}{\sqrt{2}\sigma}\right]\right]^m \ , \tag{3}$$

as shown in Fig. 1(a) for various values of m.

We now discuss the approximations implicit in Eq. (2). First, we are considering tunneling at low temperatures, so that little approximation is made by forbidding tunneling to sites of higher energy. The energy mismatch involved in the tunneling, typically a few meV, is taken up by acoustic phonons. The coupling to acoustic phonons is fairly broad,

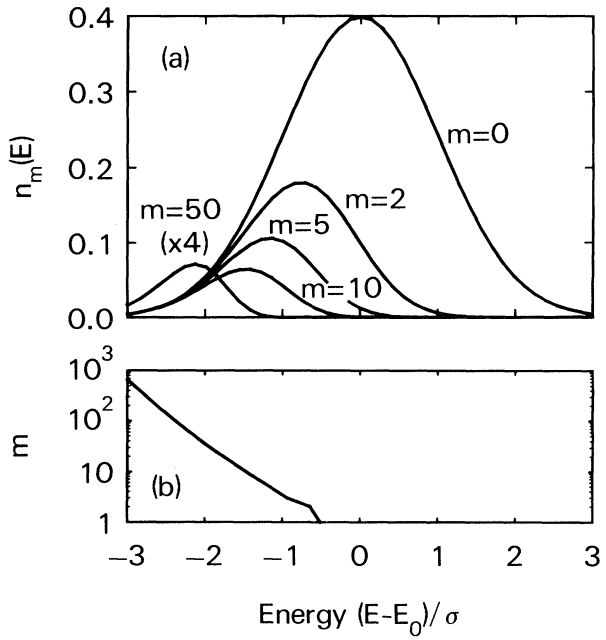

FIG. 1. (a) Density of local energy minimum states $n_m(E)$, from Eq. (3). Curves are shown for various values of m, the average number of N_x traps within the tunneling radius R_0; $m=0$ corresponds to the density of all N_x trap states. (b) Peak position vs m for the family of curves shown in (a).

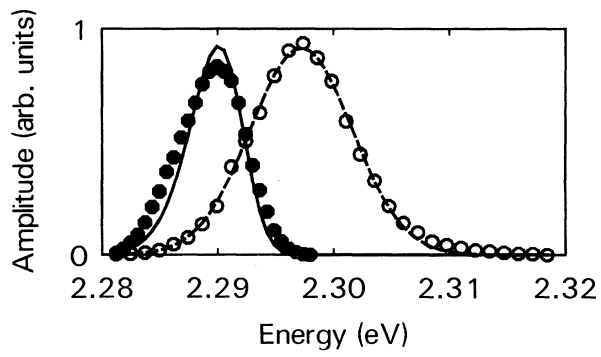

FIG. 2. cw excitation and emission spectra for $GaAs_{1-x}P_x$:N, $x \cong 0.96$, $[N] \cong 10^{18}$ cm^{-3}, $T=2$ K. The excitation spectrum was monitored in the LO phonon replica at 2.240 eV. The excitation spectrum (open circles) was fitted to a Gaussian (dashed line). This Gaussian was used to fit the emission data (filled circles) from Eq. (3). Best fit (solid line) was found for $m=14$.

as seen[10] in the acoustic phonon replica of N_x luminescence in GaP:N. Thus little variation is expected in ν_0 with tunneling energy mismatch. Next, it was assumed that the tunneling cuts off sharply at the tunneling radius R_0 when, in fact, the tunneling decays exponentially with distance. This approximation is valid because $n_m(E)$ varies slowly with m, as seen in Fig. 1(b), where the peak of $n_m(E)$ is plotted as a function of m. The use of the average value of m, rather than a Poisson distribution, is valid for the same reason. We have also assumed that nearby nitrogen sites are not correlated in energy. The N_x traps are about 100 Å apart, while extended x-ray absorption fine-structure studies suggest[11] that As or P clustering in GaAs $_{1-x}P_x$ which would cause such correlations disappear within at most a few lattice constants.

Another consideration is whether there are enough local energy minimum sites to avoid saturation, i.e., filling up all the minimum sites so that nonminimum sites begin to be populated. When saturation occurs, the exciton line shape will become thermalized. Now the proportion of all trap sites which are local energy minimum sites is $\int_{-\infty}^{\infty} n_m(E)dE = (m+1)^{-1}$. [This result is true regardless of the shape of $n_0(E)$.] For example, for $m=9$, 10% of the trap sites are local energy minimum sites. Thus, for reasonable values of m (<100) and ordinary excitation levels, no saturation will occur.

COMPARISON TO EXPERIMENT

The principal result of the theory is the line shape, Eqs. (2) and (3). In Fig. 2 we show $T=2$ K cw spectra for a $GaAs_{1-x}P_x$:N sample with $x \cong 0.96$ and $[N] \cong 10^{18}$ cm^{-3}. The excitation spectrum gives the density of states $n_0(E)$, which is fitted to a Gaussian (dashed line). This Gaussian is used to find a best fit (solid line) to the luminescence line shape from Eq. (3), varying only m and the overall amplitude. The best fit is found for $m=14$. We ignore the small (<1 meV) shift[12] expected from the splitting between the $J=\frac{1}{2}$ and $J=\frac{3}{2}$ excitons. Assuming $[N]=10^{18}$ cm^{-3}, then $R_0=150$ Å. With[7] $\nu_0=10^{12}$ sec^{-1} and[12] $\tau=800$ nsec, then $a_0 \cong 22$ Å. These results agree well with the estimates of Wiesner, Street, and Wolf[7] for exciton tunneling in GaP:N.

Under pulsed excitation, the dynamics of the tunneling process have been directly observed.[5] With the excitation resonant at the peak of the N_x density of states, narrow lines are seen in the time-resolved luminescence spectra for about 1 nsec after excitation. During this time the spectrum rapidly broadens and shifts towards lower energies, as the excitons tunnel from the sites where they were resonantly created to nearby sites of lower energy. After this initial transfer, the broadening ceases but the spectral shift slowly continues. This slow shift occurs as excitons tunnel to ever more distant sites, as m slowly increases due to the increase in $R_0(t)$. Using the values found above for the cw luminescence spectrum, the peak position in the time-resolved luminescence spectra may be predicted with no further adjustable parameters. Good agreement is found between theory and experiment.

From Eq. (1), it is evident that $R_0(\tau)$ will vary slowly with alloy composition x, principally from changes[12] in the radiative lifetime τ. Ignoring this variation, the energy shift between cw excitation and emission spectra should scale linearly with the disorder broadening, which depends upon x. This scaling has been confirmed experimentally[4] over the range $0.6 \leq x \leq 1.0$. Thus the theory correctly predicts the emission line shape for at least this range of alloy concentration without changing m.

The value found of $m=14$ for the cw emission spectra explains why no NN_i luminescence is seen at low temperatures in the alloy. At the highest concentration [N] $\cong 5\times 10^{18}$ cm^{-3}, the concentration of NN_i for a given i is less than 0.1% that the N_x concentration.[6] For $m=14$, the concentration of local energy minimum sites is $\frac{1}{15}$th of the total N_x concentration, and thus the concentration of local minimum sites far exceeds the NN_i concentration. Even if the tunneling rate $N_x \rightarrow NN_i$ is as rapid as the N_x intraband

tunneling rate (and it is probably slower due to the large energy mismatch), then an exciton is very unlikely to find an NN_i site before being trapped at a local energy minimum site.

Several other observations are consistent with the idea of local energy minimum sites. Under cw excitation, small spectral changes as a function of N concentration, temperature, and excitation power have been reported.[2,13] These are consistent with a change in m, thermally activated hopping, and saturation of the local energy minimum sites, respectively.

DISCUSSION

One final problem needs to be addressed. The distribution of local energy minimum sites has been calculated in Eq. (2). We have assumed that when excitons tunnel, they will find the local energy minimum sites randomly, uncorrelated with the energy of the site. However, because the tunneling is always to lower-energy sites, this is not the case. In fact, an exciton is more likely to find a low-energy local minimum than a high-energy one. In order to determine the importance of this effect, Monte Carlo simulation of the tunneling dynamics have been performed, building in the simple assumptions leading to Eq. (2). The initial distribution of excitons was taken as $n_0(E)$, which can be realized experimentally by above band-gap excitation. The results, shown in Fig. 3, confirm that the final exciton distribution is slightly skewed to lower energies by the dynamics of the tunneling. The shift is small, however, and can be heuristically incorporated into the theory with a slight increase in R_0.

In some respects, the theory of exciton tunneling proposed here is similar to the theory of multiple trapping[14] which has been used to explain how carriers thermalize within the localized states in the band gap of amorphous semiconductors. Multiple trapping is characterized by an energy demarcation between uniformly occupied states and states in quasithermal equilibrium. This energy grows logarithmically with time. Here we have a tunneling radius which grows logarithmically with time. It is interesting to note that multiple trapping may become important in $GaAs_{1-x}P_x$:N as the temperature is raised. For $T \gtrsim 20$ K in $GaAs_{1-x}P_x$:N, NN_i luminescence has been observed,[15] and recently the rise time of the NN_i luminescence under pulsed excitation has been seen to decrease rapidly with increasing temperature.[16] At these elevated temperatures, excitons trapped at local energy minimum N_x sites may be thermally excited, either to higher-energy N_x states or to the free exciton. Eventually the exciton is retrapped, sometimes on an NN_i site. This thermally activated hopping rate increases with temperature, whence the decrease in the NN_i luminescence rise time. Further details will be published elsewhere.[16]

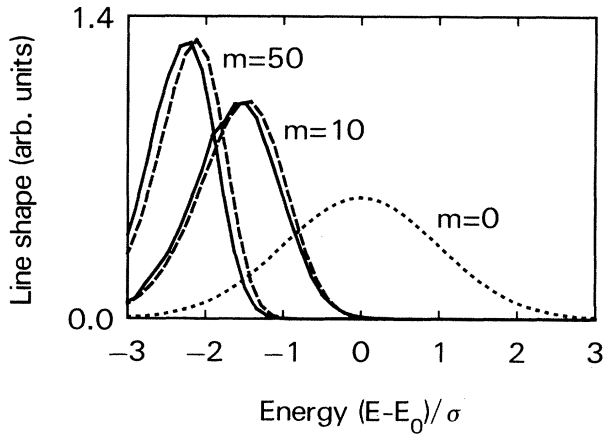

FIG. 3. Comparison between analytic theory, Eq. (3) (dashed lines), and Monte Carlo simulations (solid line) for $m = 10$ and $m = 50$. Also shown (dotted line) is the initial Gaussian density of states $n_0(E)$. All curves are normalized to the same integrated area.

CONCLUSIONS

A simple theory of exciton tunneling in $GaAs_{1-x}P_x$:N has been presented. The theory explains how disorder broadening can inhibit exciton tunneling within the N_x band, yet still permits enough tunneling to account for the shift between the emission and excitation spectra. The theory accounts for both cw and time-resolved emission line shapes, and also explains why NN_i pair emission, which dominates in heavily doped GaP:N, is not seen at low temperatures in heavily doped $GaAs_{1-x}P_x$:N.

Similar exciton tunneling has been observed for exciton bound to band-edge fluctuations in $CdS_{1-x}Se_x$,[17] and also to excitons bound[18] to quantum well-thickness fluctuations in $GaAs\text{-}GaAl_{1-x}As_x$.[19] In these cases, however, the excitons decay in about a nsec, so that there is much less time for the tunneling to occur. The theory should be applicable to these and other disordered systems (such as a-Si) where at low temperatures the dominant energy-transfer mechanism is tunneling, as opposed to thermally activated hopping.

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