Spin flip from dark to bright states in InP quantum dots

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We report measurements of the time for spin flip from dark (nonlight emitting) exciton states in quantum dots to bright (light emitting) exciton states in InP quantum dots. Dark excitons are created by two-photon excitation by an ultrafast laser. The time for spin flip between dark and bright states is found to be at most 200 ps, independent of density and temperature, below 70 K. This is much shorter than observed in other quantum dot systems.

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There has been increasing interest in the spin flip properties of quantum dots, especially relating to the study of "spintronics." Quantum dots have also been proposed as elements of quantum computers. One of the appeals of this system for quantum computing applications is the observation of very long spin flip time for carriers in quantum dots. Electron spin flip times are found to be of the order of microseconds in InGaAs dots,[1] while exciton spin flip times, which include hole spin flip, have been found to be at least several nanoseconds in InAs dots.[2]

It is tempting to view the long spin flip times observed in these sytems as an intrinsic property of quantum dots. In quantum wells and bulk semiconductors, spin flip can occur in conjunction with scattering between different **k**-states, because the valence band at finite **k** mixes different spin states. This mechanism, known as the Elliot-Yafet mechanism,[3] was found to be the dominant spin flip mechanism in exciton spin flip in GaAs quantum wells.[4] In quantum dots, however, this effect cannot occur at low temperature, because the carriers are confined to the lowest quantized state in the well. Scattering between different states can occur only along with jumps in energy which are large compared to k_BT. One therefore expects spin flip to be greatly suppressed in quantum dots.

Measurements reported here, however, as well as recent measurements by other means,[5] imply a much shorter spin flip time for excitons in InP quantum dots, much less than a nanosecond. This result is not related to coupling between the dots, since they are known to be well isolated, but may be related to the geometry of the dots.

Experimental method. As is well known, not all states in semiconductors couple directly to the optical field. In bulk semiconductors and quantum wells, there are many examples of "dark" states for which light emission is forbidden in first order due to symmetry, in contrast to "bright" states which have a dipole-allowed optical matrix element. To convert from a dark state to a bright state involves a spin flip, because the angular momentum of the two states is different.

In previous work,[4] the spin flip time from dark to bright excitons in GaAs quantum wells was measured by exciting the dark states by two-photon absorption and detecting the single-photon luminescence from bright excitons. Because the bright excitons were not excited directly by two-photon excitation, the rise time of the luminescence from the bright excitons gave a direct measurement of the spin flip time for the conversion process.

In this work we apply the same procedure to quantum dots of another III-V material InP. The quantum dots used for these experiments were a single layer of 3.0 ML InP quantum dots, with a nominal height of 3.8 nm and diameter 15.7 nm and dot density 3.2×10^{10} cm^{-2}. The gap energy of the InP is nominally 1.42 eV at low temperature. The dots are enclosed by $Ga_{0.52}In_{0.48}P$ barriers, which have band gap of 1.91 eV. As shown in earlier experiments,[7] the luminescence from the confined states of the dots occurs at photon energy of 1.805 eV, with a full width at half maximum of 0.041 eV due to the distribution of the dot size.

The symmetry properties of the quantum dots are related to those of quantum wells of the same material. Quantum wells of III-V semiconductors belong to the D_{2d} symmetry group. The topmost valence band, or heavy hole band, has Γ_7 symmetry in this group. The lowest energy excitons, created from Γ_6 conduction electrons and heavy holes, are split into an optically active Γ_5 doublet and two optically inactive "dark" exciton states with Γ_3 and Γ_4 symmetry, i.e., basis states $|j=2,m=2\rangle \pm i|j=2,m=-2\rangle$. Previous work[8] has shown that these dark states are split from the bright states by energies on the order of 100 μeV in III-V semiconductor quantum wells.

The symmetry of the quantum well is further lowered in the quantum dots, so that all of these states will become nondegenerate. Nevertheless, the quantum states in the dot will have character similar to the states of the quantum well of the same material. Single-dot spectroscopy in magnetic field has shown that the states are split into two pairs with bright and dark character, with state splitting of a few hundred μeV for dots made of a wide range of III-V and II-VI materials, including GaAs,[9,10] InAs,[11] CdSe,[12,13] and CdTe.[14] The splitting of the degenerate bright states can also be of the order of a hundred μeV.[15] The splitting of the dark and bright states in InP dots similar to ours has recently been estimated at less than 30 μeV.[6]

The dots were excited by means of two-photon absorption

using a Ti:sapphire-pumped OPO with photon energy of 0.9 eV, or 1375 nm. We used a microscope objective to focus the laser to a spot size of approximately 6 μm, and a laser pulse energy of around 1.3 nJ (100 mW at 80 MHz repetition rate) in order to obtain a good signal-to-noise ratio. The luminescence was recorded using a Hamamatsu streak camera with a *S*-1 cathode and a temporal resolution of about 10 ps.

The greatest challenge in studying the transient optical signal from the dots on the GaAs substrate is ensuring that the signal arises from direct laser excitation of the dots and not from carriers excited in the substrate which find their way to the dots. This latter process can certainly occur, as we have established by the observation that luminescence from the dots occurs even when the two-photon excitation energy is well below the lowest excited state of the dots. Substrate carriers can enter the dots by a two-step process. First, two-photon absorption can occur in the substrate, leading to free carriers, and these carriers can be excited by absorption of a third photon to energies well above the barrier height of the quantum dots. Evidence for this comes from the strong luminescence signal from the GaAs substrate which includes a tail to very high energy at early times, during the laser pulse. Some fraction of these hot carriers can then excite the quantum dots. This can occur either if hot carriers diffuse across the barriers, or if luminescence photons from the hot carriers are reabsorbed by the dots.

If this process is the dominant source of the signal, then we can not say anything about dark states in the quantum dots, because the spin of the carriers will presumably be randomized during the migration process into the dots. The rise time of the luminescence signal will give us information only about the relaxation processes which lead to this indirect excitation process.

One way to distinguish between an effect such as this and true two-photon excitation of the quantum dots uses the fact that the two-photon excitation process has a resonance at the energy of the quantum confined states, while the hot-carrier process of exciting the dots is relatively insensitive to the wavelength of the exciting light. Figure 1 shows the total intensity of the luminescence from the dots on a logarithmic scale as a function of the laser wavelength. The increase towards 1345 nm corresponds to photons with energy one half the energy of the quantum dot luminescence. As seen in this figure, well below the dot resonance, the luminescence signal from the hot carrier effect is approximately constant. We can assume that the excess signal near the resonance arises from direct two-photon excitation.

Another way to distinguish between the different processes is to note that they will have different power laws. The intensity of the signal from two-photon excitation should be proportional to the square of the laser power, while the intensity of the signal from indirect pumping of the dots hot carriers in the substrate has a much stronger intensity dependence. Figure 2 shows a comparison of the total luminescence intensity from the dots in the case of excitation at two different wavelengths. In the case of excitation at the dot resonance, the intensity dependence

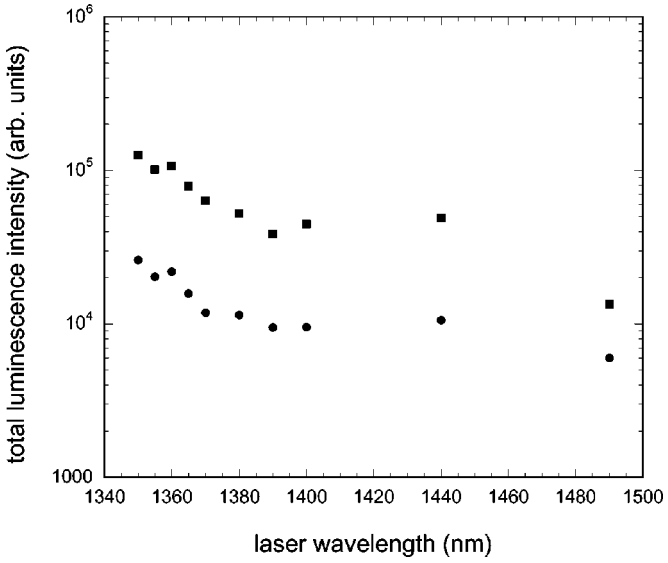

FIG. 1. Total luminescence intensity from the dots as a function of the excitation laser wavelength. Squares: 120 mW average laser power. Circles: 70 mW average laser power.

fits a power law of $I^{2.45}$, approximately equal to the expected power law of I^2. In the case of excitation well below the resonance, the power law fits a dependence of $I^{5.5}$, which is much stronger. A power law of I^3 would be expected for a straightforward three-photon process in which carriers created in the substrate absorption by two-photon absorption were excited into the dots by absorption of a third photon. The stronger power dependence reflects the fact that at high densities, the "hot phonon" effect strongly reduces carrier cooling in the substrate. This hot phonon effect was studied in detail several years ago: carrier cooling at high carrier densities is

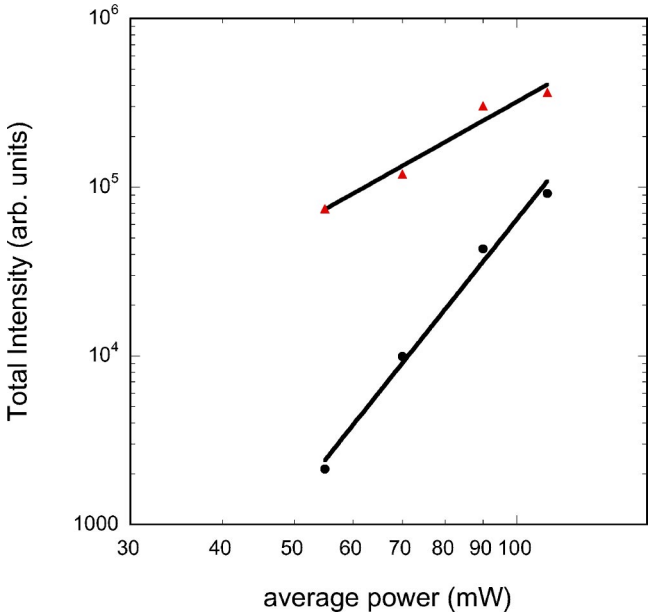

FIG. 2. Total luminescence intensity as a function of average laser power, for two different wavelengths. Circles: 1465 nm. Triangles: 1340 nm.

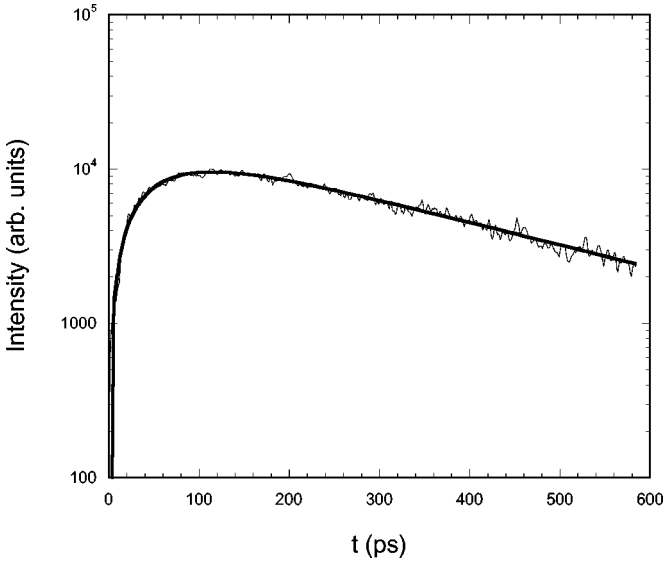

FIG. 3. Total luminescence intensity from the dots as a function of time, following two-photon excitation by a laser pulse at $t=0$. Heavy line: fit to the theory discussed in the text.

reduced since the optical phonons preferentially emitted at high carrier energy have finite lifetime. A nonthermal optical phonon occupation is built up very fast and these hot phonons strongly reabsorbed at high densities leading to a reduction of the net energy flow from the carrier into the lattice system.[16] This is verified by the fact that the high energy tail of the substrate luminescence becomes much stronger at high excitation density, and at the highest excitation density a substantial fraction of the substrate luminescence additionally overlaps the luminescence spectrum of the dots immediately after the laser pulse. The fact that the exponent in the case of resonant excitation is 2.45 instead of exactly 2 is likely due to the fact that the signal in this case is a sum of both the direct two-photon excitation signal and the signal from carriers indirectly excited from the substrate.

The difference in the power laws allows us to pick an excitation regime in which the signal from direct two-photon excitation is much stronger than that from indirect transfer of carriers from the substrate. As seen in Fig. 2, at 60 mW average power, the signal from the direct two-photon excitation process is more than a factor of ten greater than the signal from excitation of the substrate. We therefore excite the sample with laser power in this regime, instead of the highest possible laser power, in order to maximize the signal from direct two-photon excitation.

Results. Our observations indicate that there is a clear rise time of the luminescence following the nearly resonant excitation by the laser pulse. The risetime is consistent with the expected behavior for conversion of dark to bright excitons, which confirms the existence of dark states in the quantum dots. Figure 3 shows the total luminescence intensity from the dots as a function of time, at $T=10$ K, for laser power 60 mW which, as discussed in the previous section, is low enough that the effects from hot carriers in the GaAs substrate should be negligible.

The data can in general be fit to a solution of the following rate equations:

$$\frac{\partial n_1}{\partial t} = -\frac{n_1}{\tau_{12}} + \frac{n_2}{\tau_{21}} - \frac{n_1}{\tau_1},$$

$$\frac{\partial n_2}{\partial t} = \frac{n_1}{\tau_{12}} - \frac{n_2}{\tau_{21}} - \frac{n_2}{\tau_2}, \tag{1}$$

where n_1 and n_2 are the number of bright and dark excitons, respectively. The decay times τ_1 and τ_2 are the lifetimes of the excitons in their respective states, while τ_{12} and τ_{21} are times for conversion from bright states to dark and from dark to bright, respectively. Since both the bright and dark states are doublets, we assume equal degeneracy for both states.

If the recombination of the excitons is exclusively radiative, then $\tau_2=\infty$ for the dark excitons. It is possible, however, that nonradiative recombination processes give a substantial contribution to the exciton decay. Therefore, we solve these equations in two limits: for the case in which decay of the dark states is forbidden, and the case in which $\tau_1=\tau_2$, which corresponds to nonradiative recombination dominating the lifetime for both states.

In principle, τ_{12} and τ_{21} can be different, as found for quantum wells at low temperature,[4] but if the energy splitting between the states is small compared to k_BT, then these rates will be nearly the same. In the present experiments, the temperature ranged from 10 to 75 K. Assuming that the splitting of the dark and bright states is of the order of 100 μeV or less, as discussed above, the splitting is much less than k_BT, and therefore we can set $\tau_{12}=\tau_{21}=\tau$. In this case, the solution of Eqs. (1) for the initial condition $n_1(0)=0$, $n_2(0)=1$, in the case $\tau_2=\infty$, is

$$n_1(t) = \frac{\tau_1}{\sqrt{\tau^2+4\tau_1^2}}\left(e^{-t(\tau+2\tau_1-\sqrt{\tau^2+4\tau_1^2})/2\tau\tau_1} - e^{-t(\tau+2\tau_1+\sqrt{\tau^2+4\tau_1^2})/2\tau\tau_1}\right)$$
$$\equiv C(e^{-t/\tau_d} - e^{-t/\tau_r}). \tag{2}$$

Surprisingly, this solution implies that the minimum ratio of the decay time τ_d to the rise time τ_r is $5.85=(2+\sqrt{2})/(2-\sqrt{2})$, for the case $\tau=2\tau_1$. For all other choices of the time constants, the ratio of the decay time to the rise time is larger than this. This shows that when there are dark states with long lifetime in the system, it is improper to interpret the rise time of the luminescence as the spin flip time and the decay time as the radiative lifetime. Because of the interconversion between the states, both time scales depend on both τ and τ_1. Within the experimental uncertainty, our data at low T give this ratio, which implies that $\tau\simeq 2\tau_1$, and in general, that τ is longer than τ_1.

When the ratio deviates from this minimum value, there are two possible solutions for τ and τ_1 given the experimental values of τ_r and τ_d, as follows:

TABLE I. Time constants determined by the fits of the data to the model discussed in the text, in the case $\tau_2=\infty$. The ranges of the values of τ and τ_1 given here represent all possible solutions of Eq. (3) using values of τ_r and τ_d which fall within the ranges of uncertainty of their fit values.

	10 K	20 K	40 K	75 K
rise time (ps)	55±9	53±10	54±8	45±8
decay time (ps)	297±15	299±16	349±17	502±22
τ (ps)	209±27	218±31	255±44	445±36
τ_1 (ps)	71±9	68±13	73±16	50±11

$$\tau_1 = \frac{\tau_d + \tau_r - \sqrt{\tau_d^2 - 6\tau_d\tau_r + \tau_r^2}}{4},\ \tau = \frac{\tau_d + \tau_r + \sqrt{\tau_d^2 - 6\tau_d\tau_r + \tau_r^2}}{2}, \tag{3}$$

or

$$\tau_1 = \frac{\tau_d + \tau_r + \sqrt{\tau_d^2 - 6\tau_d\tau_r + \tau_r^2}}{4},\ \tau = \frac{\tau_d + \tau_r - \sqrt{\tau_d^2 - 6\tau_d\tau_r + \tau_r^2}}{2}. \tag{4}$$

We take the former solution here, which is consistent with the recombination time τ_1 essentially independent of the temperature, and the spin flip time τ longer than τ_1 in all cases. Table I gives the temperature dependence of the values deduced from these fits. As seen in this table, the conversion time from dark to bright states remains approximately 200 ps at low temperature. If the alternate solution (4) is taken, then the implied spin flip time drops to tens of picoseconds while the radiative recombination time becomes significantly longer at $T=75$ K.

So far we have examined the case when $\tau_2=\infty$, i.e., when the dark states have much longer lifetime than the bright states. If we take the limit that both are dominated by nonradiative recombination with the same lifetime $\tau_1=\tau_2$, then the solution to Eqs. (1) is simply

$$n_1(t) = \frac{1}{2}(e^{-t/\tau_1} - e^{-t/\tau}), \tag{5}$$

and we are justified in treating the rise time as the spin flip time and the decay time as the recombination lifetime. In this case, the implied spin flip times are even shorter than deduced above, equal to the fit rise times in the range of 50 ps. These measurements therefore imply an *upper bound* on the spin flip times of around 200 ps at low temperature.

We want to stress that the model presented here implies that if long-lifetime dark states exist, the decay of the dot luminescence is dominated by the interconversion of the dark and bright states. Long after the laser pulse, the luminescence decay time for single-photon excitation will be the same as that given in Eq. (2) for two-photon excitation. According to this equation, the decay time τ_d of the photoluminescence will be equal to $2\tau_1$ in the limit that the spin flip time is much shorter than the radiative lifetime; in the limit of long spin flip time, the decay time τ_d will be essentially equal to the spin flip time τ, not τ_1. This effect of interconversion of bright and dark excitons, although discussed in detail for the case of quantum wells,[17] has been neglected in several previous publications; for example, in Refs. 18–20 the photoluminescence decay time was taken simply as the radiative decay time while as seen here, the decay rate even at late times is in general a function of the spin flip time from dark states. In Ref. 18, the photoluminescence lifetime of excitons in InP quantum dots was studied for the first time for resonant excitation. This lifetime was found to be independent of excitation density and temperature. The results were discussed and compared with results obtained with quantum wells without considering the contribution of dark exciton states, which are populated via spin flip and which might act as an exciton reservoir, to the measured photoluminescence lifetime. Later, similar experiments with resonant excitation of self-assembled InGa/GaAs dots were performed.[19] Again the measured photoluminescence lifetime was interpreted as being directly the lifetime of the excitons and the possibility that dark exciton states might act as an exciton reservoir was not taken into account. Bayer *et al.*[20] measured the inhibition and enhancement of the exciton emission of quantum dots in structured microresonators. They found a decreased lifetime for on-resonance condition and an increased lifetime for off-resonance conditions. The results were theoretically analyzed not taking into account the dark states acting as a possible reservoir.

We find no power dependence of the spin flip time τ. This is not surprising, since the excitation density is so low that it is unlikely that there is more than one electron per dot. In this case, each dot relaxes individually.

The most likely reason for the variation in the time constants at $T=75$ K is that at high temperature, carriers are excited into higher quantized states, which lie approximately 10 meV above the lowest state[21] so that our simple two-state model breaks down. At low temperature, the time constants are essentially independent of temperature.

The short spin flip time is surprising, because as discussed above, previous studies have found a dramatically slower rate for spin flip in quantum dots at low temperature. As mentioned above, however, another study of InP dots[5] has found a very short time constant for depolarization of the luminescence from the dots, less than 100 ps, following excitation with circular polarized light. This short lifetime was interpreted by the authors of Ref. 5 as due to interference of the light emitted from the ensemble of quantum dots with large inhomogeneous broadening. That explanation does not apply to the experiments reported here, however, because our method of measuring the time scale for spin flip from dark to bright excitons is insensitive to the inhomogeneous broadening of the ensemble. A possible explanation for the large range of spin flip times may come from the differences in geometry of the dots. Woods, Reinecke, and Lyanda-Geller[22] have calculated the rate of spin flip in dots as a function of the dot geometry, for two possible mechanisms, acoustic phonon emission and interface ripples, analogous to surface acoustic waves on the interface between

the dots and the barriers. They found a very strong size dependence; in particular, the height of our quantum dots of 3.8 nm lies in the range at which they found an extremely stiff increase of the rate of spin flip with decreasing size.

Dark states play an important role in the relaxation of bright excitons in quantum dots, controlling the observed luminescence decay rate. We find a nearly constant rate of conversion from bright to dark excitons in InP quantum dots at low temperature, approximately 200 ps. The results from InP show that it cannot be generally assumed that spin flip times are always long in quantum dots.

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