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 (non-light 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 approximately 200 ps, independent of density and temperature below 70 K. This is much shorter than observed in other quantum dot systems. The rate of decay of the luminescence intensity, approximately 300 ps, is not simply equal to the radiative decay rate from the bright states, because the rate of decay is limited by the rate of conversion from dark excitons into bright excitons. The dependence of the luminescence decay time on the spin flip time is a general effect that applies to many experiments.
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]. Measurements of the dephasing rate, which are sensitive to the total rate of all scattering processes, including spin flip, have found dephasing times for excitons in quantum dots of hundreds of picoseconds [3,4].

It is tempting to view the long spin flip times observed in these systems 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 [5], was found to be the dominant spin flip mechanism in exciton spin flip in GaAs quantum wells [6]. 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 \( k_B T \). One therefore expects spin flip to be greatly suppressed in quantum dots.

Measurements reported here, however, as well as recent measurements by other means [7], 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 [6], 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. A priori, it is not obvious that dark states exist in the dots, because the change in symmetry properties may mean that all the confined states have dipole coupling to the light field. If they do exist, we should observe a rise time of the luminescence following the laser pulse which creates the dark excitons, just as in the case of dark states in quantum wells. Having proven the existence of dark states in this way, we can then determine the spin flip time for conversion from dark to bright states.

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 $3.2 \times 10^{10}$ 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 [9], 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 $\Gamma_7$ symmetry in this group. The lowest energy excitons, created from $\Gamma_6$ conduction electrons and heavy holes, are split into an optically-active $\Gamma_5$ doublet and two optically inactive “dark” exciton states with $\Gamma_3$ and $\Gamma_4$ symmetry, i.e. basis states $|j = 2, m = 2\rangle \pm i|j = 2, m = -2\rangle$. Previous work [10] has shown that these dark states are split from the bright states by energies on the order of $100 \mu eV$ 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 at with bright and dark character, with state splitting of a few hundred $\mu eV$ for dots made of a wide range of III-V and II-VI materials, including GaAs [11,12], InAs [13], CdSe [14,15], and CdTe [16]. The splitting of the degenerate bright states can also be of the order of a hundred $\mu eV$ [17]. The splitting of the dark and bright states in InP dots similar to ours has recently been estimated at less than $30 \mu eV$ [8].

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 $\mu m$, 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 like 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. Fig. 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. Fig. 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 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 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 [18]. 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. Fig. 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 fit to the data of Fig. 3 is a solution of a simple set of rate equations,

$$\frac{\partial n_1}{\partial t} = -\frac{n_1}{\tau_{12}} + \frac{n_2}{\tau_{21}} - \frac{n_1}{\tau_0}$$

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

(1)
where \( n_1 \) and \( n_2 \) are the number of bright and dark excitons, respectively. The decay time \( \tau_0 \) is the radiative lifetime of the excitons in the bright state, while \( \tau_{12} \) and \( \tau_{21} \) 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. In principle, \( \tau_{12} \) and \( \tau_{21} \) can be different, as found for quantum wells at low temperature [6], but if the energy splitting between the states is small compared to \( k_B T \), then these rates will be nearly the same. In the present experiments, the temperature ranged from 10 K to 75 K. Assuming that the splitting of the dark and bright states is of the order of 100 \( \mu eV \) or less, as discussed above, the splitting is much less than \( k_B T \), and therefore we can set \( \tau_{12} = \tau_{21} = \tau \).

In this case, the solution of the equations (1) for the initial condition \( n_1(0) = 0, n_2(0) = 1 \), is

\[
\begin{align*}
n_1(t) &= \frac{\tau_0}{\sqrt{\tau^2 + 4\tau_0^2}} \left( e^{-t\left(\tau + 2\tau_0 - \sqrt{\tau^2 + 4\tau_0^2}\right)/2\tau_0} - e^{-t\left(\tau + 2\tau_0 + \sqrt{\tau^2 + 4\tau_0^2}\right)/2\tau_0} \right) \\
&\equiv C \left( e^{-t/\tau_d} - e^{-t/\tau_r} \right)
\end{align*}
\]

Surprisingly, this solution implies that the minimum ratio of the decay time \( \tau_d \) to the rise time \( \tau_r \) is \( 5.85 = (2 + \sqrt{2})/(2 - \sqrt{2}) \), for the case \( \tau = 2\tau_0 \). 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 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 \( \tau \) and \( \tau_0 \). Within the experimental uncertainty, our data at low \( T \) give this ratio, which implies that \( \tau \simeq 2\tau_0 \), and in general, that \( \tau \) is longer than \( \tau_0 \).

When the ratio deviates from this minimum value, there are two possible solutions for \( \tau \) and \( \tau_0 \) given the experimental values of \( \tau_r \) and \( \tau_d \), as follows:
\[ \tau_0 = \frac{\tau_d + \tau_r - \sqrt{\tau_d^2 - 6\tau_d \tau_r + \tau_r^2}}{4}, \quad \tau = \frac{\tau_d + \tau_r + \sqrt{\tau_d^2 - 6\tau_d \tau_r + \tau_r^2}}{2} \] (3)

or

\[ \tau_0 = \frac{\tau_d + \tau_r + \sqrt{\tau_d^2 - 6\tau_d \tau_r + \tau_r^2}}{4}, \quad \tau = \frac{\tau_d + \tau_r - \sqrt{\tau_d^2 - 6\tau_d \tau_r + \tau_r^2}}{2}. \] (4)

We take the former solution here, which is consistent with the radiative recombination time \( \tau_0 \) essentially independent of the temperature, as expected, and the spin flip time \( \tau \) longer than \( \tau_0 \) in all cases. Table 1 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.

We want to stress that the model presented here implies that even in the case of resonant single-photon excitation, 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 Equation (2) for two-photon excitation. According to this equation, the decay time \( \tau_d \) of the photoluminescence will be equal to \( 2\tau_0 \) 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 \( \tau_d \) will be essentially equal to the spin flip time \( \tau \), not \( \tau_0 \). This effect of interconversion of bright and dark excitons, although discussed in detail for the case of quantum wells [19], has been neglected in several previous publications; for example, in Refs. [20–22] 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.
The radiative decay rates found here are consistent with the strong localization of the carriers which extends the recombination time. Typical intrinsic decay times for quantum wells are a few tens of picoseconds [23,24], while the recombination time found for the dots in these experiments is around 70 ps, which corresponds to a total radiative decay time of 140 ps in the limit of fast spin flip.

We find no power dependence of the spin flip time $\tau$. 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 [25] 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 [7] has found a very short time constant for depolarization of the luminescence from the dots following excitation with circular polarized light. This short lifetime was interpreted by the authors of [7] 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 [26] 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 a strongly increasing 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.

[1] T. Fujisawa, D.G. Austing, Y. Tokura, Y. Hirayama, and S. Tarucha, Phys. Rev. Lett. 88, 236802 (2002).

[2] M. Paillard, X. Marie, P. Renucci, T. Amand, A. Jbeli, and J.M. Gérard, Phys. Rev. Lett. 86, 1634 (2001).

[3] D. Birkedal, K. Leosson, and J. M. Hvam, Phys. Rev. Lett. 87, 227401 (2001).

[4] P. Borri, W. Langbein, S. Schneider, U. Woggon, R. L. Sellin, D. Ouyang, and D. Bimberg Phys. Rev. Lett. 87, 157401 (2001).

[5] G. L. Bir, A. G. Aronov, and G. E. Pikus, Zh. Éksp. Teor. Fiz. 60, 1382 (1975). [Sov. Phys. JETP 42, 705 (1976)].
[6] D.W. Snoke, W.W. Rühle, K. Köhler, and K. Ploog, Physical Review B 55, 13789 (1997).

[7] I.V. Ignatiev, I.Ya. Gerlovin, M. Ikezawa, V.K. Kalevich, S.Yu. Verbin, and Y. Masumoto, Physica E 17, 361 (2003); I.A. Yugova, I.Ya. Gerlovin, I.V. Ignatiev, S.Yu. Verbin, and Y. Masumoto, Proc. 14th Indium Phosphide and Related Materials Conference (2002), p. 71.

[8] I.A. Yugova, I.Ya. Gerlovin, V.G. Davydov, I.V. Ignatiev, I.E. Kozin, H.W. Ren, M. Sugisaki, S. Sugou, and Y. Masumoto, Phys. Rev. B 66, 235312 (2002).

[9] M. K. Zundel, P. Specht, K. Eberl, N. Y. Jin-Phillipp, and F. Phillipp, Appl. Phys. Lett. 71, 2972 (1997).

[10] E. Blackwood, M. J. Snelling, R. T. Harley, S. R. Andrews, and C. T. B. Foxon, Phys. Rev. B 50, 14246 (1994).

[11] E.L. Ivchenko, Physica Status Solidi (a) 164, 487 (1997).

[12] A.G. Steffan, and R.T. Phillips, Physica Status Solidi (a) 190, 541 (2002).

[13] M. Bayer, G. Ortner, O. Stern, A. Kuther, A. A. Gorbunov, A. Forchel, P. Hawrylak, S. Fafard, K. Hinzer, T. L. Reinecke, S. N. Walck, J. P. Reithmaier, F. Klopf, and F. Schäfer, Phys. Rev. B 65, 195315 (2002).

[14] M. Nirmal, D.J. Norris, M. Kuno, M.G. Bawendi, Al.L. Efros, and M. Rosen, Phys. Rev. Lett. 75, 3728 (1995).

[15] Al.L. Efros, M. Rosen, M. Kuno, M. Nirmal, D.J. Norris, and M. Bawendi, Phys. Rev. B 54, 4843 (1996).

[16] L. Besombes, K. Kheng, and D. Mariou, Phys. Rev. Lett. 85, 425 (2000).
[17] M. Sugisaki, H.-W. Ren, S. Nair, K. Nishi, S. Suguo, T. Okuno, and Y. Masumoto, Phys. Rev. B 59, R5300 (1999).

[18] X. Q. Zhou, H. M. van Driel, W. W. Rühle, and K. Ploog, Phys. Rev. B 46, 16148 (1992).

[19] A. Vinattieri, J. Shah, T. C. Damen, D. S. Kim, L. N. Pfeiffer, M. Z. Maialle, and L. J. Sham, Phys. Rev. B 50, 10868, (1994).

[20] W. W. Rühle, A. Kurtenbach and K. Eberl, Il Nuovo Cimento 17, 1305 (1995).

[21] M. Paillard, X. Marie, E. Vanelle, T. Amand, V. K. Kalevich, V. M. Ustinov, and N. N. Ledentsov, Appl. Phys. Lett. 76, 76 (2000).

[22] M. Bayer, F. Weidner, A. Larionov, A. McDonald, A. Forchel, and T. L. Reinecke, Phys. Rev. Lett. 86, 3168 (2001).

[23] L. C. Andreani, F. Tassone, and F. Bassani, Solid State Comm. 77 641 (1991).

[24] B. Deveaud, F. Clerot, N. Roy, K. Satzke, B. Sermage, and D. S. Katzer, Phys. Rev. Lett. 67, 2355 (1991).

[25] C. Ulrich, S. Ves, A. R. Goñi, A. Kurtenbach, K. Syassen, and K. Eberl, Phys. Rev. B 52, 12212 (1995).

[26] L. M. Woods, T. L. Reinecke, and Y. Lyanda-Geller, Phys. Rev. B 66, 161318 (2002).
|                        | 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  |
| $\tau$ (ps)            | 209 ± 27  | 218 ± 31  | 255 ± 44  | 445 ± 36  |
| $\tau_0$ (ps)          | 71 ± 9    | 68 ± 13   | 73 ± 16   | 50 ± 11   |

**TABLE I.** Time constants determined by the fits of the data to the model discussed in the text.

The ranges of the values of $\tau$ and $\tau_0$ given here represent all possible solutions of (3) using values of $\tau_r$ and $\tau_d$ which fall within the ranges of uncertainty of their fit values.
FIG. 1. Total luminescence intensity from the dots as a function of the excitation laser wavelength.
FIG. 2. Total luminescence intensity as a function of average laser power, for two different wavelengths. Squares: 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.