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Exciton spin dynamics in ZnO epilayers

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We used time-resolved optical orientation experiments to study the low temperature spin dynamics of a ZnO epilayer. The sample shows a circular polarisation of the donor-bound exciton of 11% with a decay time of 275 ps. A very narrow spectral dependence of the initial polarisation and a rapid decrease of the polarisation decay time with temperature are also observed.

1 Introduction ZnO is a wide band gap semiconductor with a very large exciton binding energy (~60 meV) [1]. Its material properties make it both very convenient for ultra-violet devices and a potential candidate for spintronic applications. For this latter reason, it is essential to understand the physics of the phenomena governing the exciton spin dynamics. The electron spin properties have recently been investigated in n-type ZnO structures [5]. However, to the best of our knowledge, the exciton spin dynamics has not been studied yet. Optical orientation experiments are indeed difficult to implement in ZnO because the small spin-orbit interaction (~16 meV [1]) requires an almost resonant excitation of the excitons.

2 Experimental set-up and sample characteristics The sample under study is a high quality, nominally undoped, 1.1 μm thick epilayer grown on an α-sapphire (0001) substrate using an rf-plasma-assisted MBE system [2].

The time-resolved optical orientation photoluminescence (PL) is used as a technique to investigate the spin properties of the ZnO excitons. The principle is to transfer the angular momentum of the excitation photons to the photogenerated carriers by using circularly polarised light. By measuring the maximum degree of the PL circular polarisation and its decay time it is possible to determine the dynamical properties of the carriers spin.

The excitation source is provided by a mode-locked frequency-doubled Ti:Sa laser, with a 1.5 ps pulse width and a repetition frequency of 80 MHz. The right circular polarized (σ^+) laser beam is focused onto the cooled sample (T = 20 K) to a 100 μm diameter spot with an average power P_{exc} = 5 mW. The PL intensity is afterward circularly analysed either co- and counter-polarised (I^+, I^-) with respect to the excitation laser and dispersed by an imaging spectrometer. The temporal and spectral properties of the signal are detected by a S1 photocathode streak camera with an overall time-resolution of 8 ps. The degree of circular polarisation of the luminescence is then defined as $P_c = (I^+-I^-)/(I^++I^-)$.

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3 Experimental results Figure 1a presents the time-integrated PL spectrum at low temperature of the ZnO epilayer as a function of the excitation power. The energies and the natures of the spectral lines of interest for this study are indicated. The power laws of the integrated intensity of these lines and their temperature dependence (not shown here) allow us to unambiguously assign the lines at 3.375 meV, 3.363 meV and 3.359 meV to the free exciton A (FX_A) and to the FX_A excitons bound to two different donor species ($D^0{}_1X_A$, $D^0{}_2X_A$), respectively.

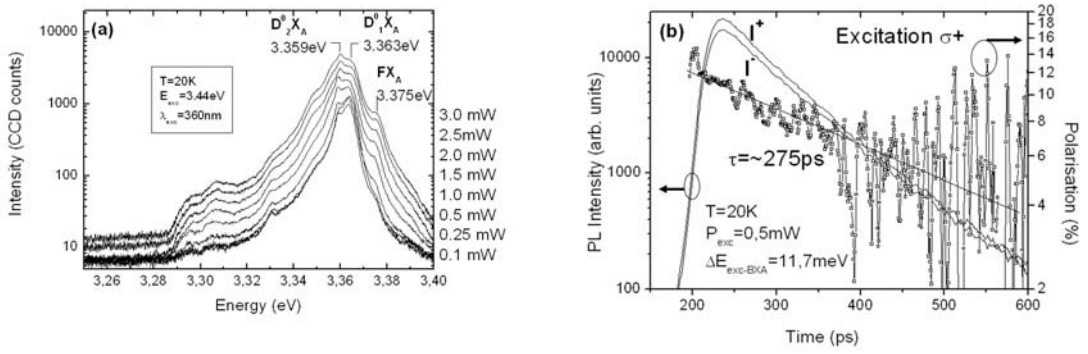

Fig. 1 (a) Low temperature time-integrated, power dependent PL spectra of the ZnO epilayer. (b) Time evolution of the circular luminescence components (I^+) and (I^-) after a (σ^+) polarised excitation. The circular polarisation (right axis) is also displayed. The straight line is a fit to the polarisation decay time with τ = 275 ps. The detection energy is at the $D^0{}_2X_A$ energy position while the excitation laser is tuned 11.7 meV above the detection.

Figure 1b shows the time evolution of the T=20K co-polarised (I^+) and counter-polarised (I^-) luminescence intensity components detected at the $D^0{}_2X_A$ energy, with the corresponding degree of circular polarisation. The excitation energy is E_{ex} = 3.371 meV i.e. ~12 meV above the detection energy, with a time averaged power P_{ave} = 0.5 mW. The initial polarisation observed is P(0)~10% which decays with a time constant τ = 275ps. Detecting on the FX_A we have not observed any polarisation of the photoluminescence after 30 ps from the laser excitation. This suggests that, contrary to the bound exciton, the spin relaxation time of the exciton in the free phase is very fast. This short exciton spin relaxation time has been indeed recently observed in GaN [3, 4].

In Fig. 2a are shown the low temperature (T = 20 K) spectral dependence of the $D^0{}_2X_A$ polarisation (full square) and the respective time integrated intensity (open square) together with the position of the detection energy and of the A and B excitons (FX_A, FX_B). The excitation energy has been varied from a minimum energy difference of 5 meV from the $D^0{}_2X_A$ up to energies about 40 meV higher. We measure a very narrow peak of polarisation with a maximum value P_{max} = 12% at 12 meV from the $D^0{}_2X_A$. The degree of polarisation then decays to zero when the excitation energy is higher than the FX_B position. This reflects the fact that with a σ^+ excitation above this energy, we generate an equal number of spin up and spin down carriers, as expected by theoretical selection rules and neglecting the spin scattering processes.

In Fig. 2b (main graph) we present the temperature dependence (from T = 20 K to 35 K) of the $D^0{}_2X_A$ polarisation decay time. The inset of Fig. 2b shows, as an example, three corresponding experimental curves of the time evolution of the polarisation degree at T = 20 K, 22 K and 34 K. The polarisation decay time drops drastically when increasing the temperature by a few Kelvin.

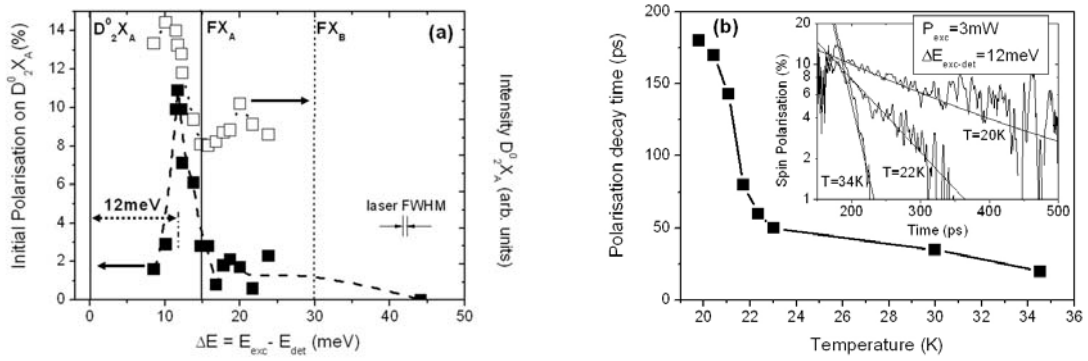

Fig. 2 (a) Spectral dependence of the excitation energy for the $D^0{}_2X_A$ polarisation (full square) and intensity (open square). (b) Temperature dependence of the $D^0{}_2X_A$ spin decay time. Inset: corresponding polarisation time evolution of the $D^0{}_2X_A$ for three sample temperatures.

To discuss the nature of the observed polarisation, we note that an exciton bound to a donor consists of a singlet of electrons and a hole. Therefore, the detected polarisation is a direct measurement of the orientation of the hole spin. As a confirmation of this fact, earlier measurements of the electron spin dynamics in ZnO have shown that the electron possesses a very long and robust spin relaxation time up to room temperature [5]. The extreme sensitivity of the polarisation decay time with temperature measured in this work is thus a further argument in favour of the fact that the observed polarisation is due to the hole spin. It is as well interesting to note that the peak of polarisation and intensity of the $D^0{}_2X_A$ (Fig. 2a) occurs at an excitation energy ~3 meV below the FX_A which suggests that the exciton-polaritons might play a significant role in the spin dynamics of the excitons [1]. This should be expected for ZnO as it is a strongly polar material with large oscillator strength.

To interpret the rapid temperature evolution of the polarisation decay time we first observe that its low temperature activation energy is close to the binding energy of the $D^0{}_2X_A$ (15 meV). This means that above 20 K the excitons trapped by a donor can gain sufficient energy to be released as free excitons. The fast decrease of the polarisation decay time is a reflection of the larger time that the exciton spends in the free phase where it can efficiently lose its spin orientation as supported by the absence of a measurable polarisation on the FX_A luminescence.

In conclusion, we have measured the time-resolved circularly polarised photoluminescence of ZnO which unambiguously demonstrates the optical orientation of the donor-bound exciton complexes. The spectral dependence of the $D^0{}_2X_A$ polarisation and intensity and the material properties of ZnO suggest that the exciton-polariton picture might help in the understanding of the ZnO exciton spin dynamics.

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