The coherent optical response from 140 nm and 65 nm thick ZnO epitaxial layers is studied using transient four-wave-mixing spectroscopy with picosecond temporal resolution. Resonant excitation of neutral donor-bound excitons results in two-pulse and three-pulse photon echoes. For the donor-bound A exciton (D$^0$X$_A$), at temperature of 1.8 K we evaluate optical coherence times $T_2 = 33–50$ ps, corresponding to homogeneous linewidths of 13–19 µeV, about two orders of magnitude smaller as compared with the inhomogeneous broadening of the optical transitions. The coherent dynamics is determined mainly by the population decay with time $T_1 = 30–40$ ps, while pure dephasing is negligible in the studied high quality samples even for strong optical excitation. Temperature increase leads to a significant shortening of $T_2$ due to interaction with acoustic phonons. In contrast, the loss of coherence of the donor-bound B exciton (D$^0$X$_B$) is significantly faster ($T_2 = 3.6$ ps) and governed by pure dephasing processes.

The optical properties of ZnO are of great interest for applications in ultraviolet (UV) light emitting devices and other photonic devices. The main feature of this is the large exciton binding energy of $\sim 60$ meV, so that exciton emission occurs even at room temperature. Another remarkable property is the large exciton oscillator strength resulting in short optical lifetimes, which could be useful in applications requiring fast coherent control.

So far, the coherent optical properties of ZnO were studied on free excitons with short coherence times up to few ps. Optical excitation with spectrally broad femtosecond pulses was implemented and, consequently, quantum beats between various exciton states as well as strong many-body interactions were demonstrated. For exciton complexes bound to impurities, e.g., quantum-confined excitons, long-lived coherence is expected. In order to study distinct states exhibiting long coherence times, four-wave-mixing (FWM) spectroscopy is preferentially performed with resonant excitation of the exciton complex of interest using spectrally narrow pulses, even though the time resolution is reduced thereby. Furthermore, to overcome the large inhomogeneity of exciton transitions, which represents another intrinsic property of ZnO leading to sub-ps decay of macroscopic polarization, photon echo-based techniques are the best choice for studying the coherent dynamics of excitons.

In this letter, we demonstrate that for resonant optical excitation of the donor-bound A and B excitons in ZnO epitaxial layers with ps pulses the coherent response is given by photon echoes. The decay of the photon echo signals allows one to determine intrinsic properties of the single donor bound excitons, such as the coherence time $T_2$ and population decay time $T_1$. At temperature of 1.8 K, the coherence time of the A bound exciton (D$^0$X$_A$) is in the range of several tens of ps, corresponding to a homogeneous linewidth of about 10-20 µeV, which is two orders of magnitude smaller than the inhomogeneous broadening of D$^0$X$_A$. Our findings demonstrate that the D$^0$X$_A$ in ZnO represents a promising two-level system which may be used for ultrafast optical control. In contrast, the decoherence of D$^0$X$_B$ occurs one order of magnitude faster, while the population decay is approximately the same. In addition, we show that a temperature increase leads to significant shortening of the coherence times due to interactions with phonons.

Samples and method. For our study of localized exciton states in bulk ZnO, we used two ZnO epilayers grown by plasma-assisted molecular-beam epitaxy on c-plane (0001) sapphire substrates. Sample I fabricated in Berlin (ZMO1031) is a 140 nm thick ZnO epitaxial layer surrounded by Zn$_{0.9}$Mg$_{0.1}$O layers with thicknesses of 100 nm and 1 µm from top and bottom, respectively. Sample II fabricated in Paderborn (ZnO-385) is a 65 nm thick ZnO layer separated from the substrate by a 45 nm thick buffer of low-temperature grown ZnO. Both samples are deposited with a 1-2 nm-thick MgO nucleation layer.

The coherent optical response was measured using a three-pulse degenerate FWM setup in reflection geometry. The samples were inserted in a helium bath cryostat and cooled down to 1.8 K. As laser source we used a Ti:Sapphire laser Mira-900 with pulse repetition rate of 75.75 MHz combined with an external second-harmonic generation unit which delivered frequency-doubled pulses in ultraviolet spectral range with 1.3 ps-duration.
third pulse was collinear with the second one, respectively, in a spot of about 250 µm diameter. The intensity of the excitation pulses was kept below 10 mW per beam ensuring the coherent response to be in the χ(3) regime. The FWM signal was detected along the k_{FWM} = 2k_2 - k_1 direction. To detect the weak FWM signal, optical heterodyning and interference with a reference laser pulse were exploited [16, 17]. Optical heterodyning was accomplished with two acousto-optical modulators (AOMs) acting as optical frequency shifters. The optical frequency of the first pulse was shifted to \( f_1 = f_0 - 81\text{MHz} \) with the first AOM, while the optical frequency of the reference pulse separated by \( \tau_{\text{ref}} \) from the first pulse was shifted to \( f_{\text{Ref}} = f_0 + 80\text{MHz} \) with the second AOM. Thus, the optical frequency of the FWM signal is given by \( f_{\text{FWM}} = 2f_0 - f_1 = f_0 + 81\text{MHz} \). The FWM and the reference beams were mixed in a silicon photodetector and the modulus of the cross-correlation of the FWM optical field with the reference pulse field, \( I_{\text{det}} \), was detected at 1 MHz frequency by a fast lock-in amplifier. Additionally, the first beam was modulated by an optical chopper at 1 kHz frequency, at which synchronous detection by a slow lock-in amplifier was done. All beams were linearly co-polarized.

**Experimental results.** Figures 1(b) and 1(c) show FWM spectra measured at \( \tau_{\text{ref}} = 2\tau_{12} \) on both samples for short \( \tau_{12} \) delays of 2.7 ps and 3.3 ps. Four main transitions are seen in the spectra associated with the free A exciton (X_A), free B exciton (X_B), neutral donor-bound A exciton (D^0X_A), and neutral donor-bound B exciton (D^0X_B), in good correspondence with the absorption spectrum measured on sample I [18]. Additional transition is seen for sample I at \( \sim 3.369\text{ eV} \) (about 11.7 meV above D^0X_A), as previously observed in photoluminescence excitation spectra and attributed to an excited d-state of the donor-bound exciton A (D^0X_A) [18–20]. The exciton resonances in the 65 nm ZnO layer are shifted by 2.0 – 3.7 meV relative to those in the 140 nm layer, which we attribute to presence of residual strain in the samples [21]. The free A and B exciton signals decay extremely fast on sub-ps timescale, so that they are already significantly damped in FWM when measured at \( \tau_{12} = 3.3\text{ ps} \). We estimate the coherence times of these free excitons to be below 1 ps, in line with previous studies [3, 11]. Donor-bound excitons decay significantly slower so that they can be studied in detail with ps transient photon echo spectroscopy.

FWM signal from D^0X_A in form of photon echoes was observed on both samples. Figure 2(a) displays the
FWM amplitude transient measured on sample II in the three-pulse echo experiment at $\tau_{12} = \tau_{23} = 6.67$ ps. This transient is composed of two echo pulses located at the times of the PE ($2\tau_{12} = 13.3$ ps) and the SPE ($2\tau_{12} + \tau_{23} = 20$ ps). The temporal profiles of PE and SPE are well fitted with Gaussians with a full width at half maximum (FWHM) of 2.1 ps. In this case the excited ensemble is defined by the laser spectrum, i.e., the latter is narrower than the inhomogeneous width of the optical transitions. Figure 2(b) shows PE spectra measured at $\tau_{12} = 26.7$ ps for sample I and 13.3 ps for sample II. The spectral resolution in these measurements is given by the 1.7 meV FWHM of the laser spectrum, shown by the dashed line. Accordingly in sample I the inhomogeneous broadening of optical transitions is smaller, which we attribute to weaker strain gradients across the ZnO epilayer due to presence of the intermediate ZnMgO buffer layer.

To measure the $T_2$ and $T_1$ times of the donor bound excitons, we either vary the $\tau_{12}$ delay with PE amplitude detection or the $\tau_{23}$ delay with SPE amplitude detection. These data are summarized in Fig. 3. D$^0$X$_A$ PE decays measured on both samples in the two-pulse echo experiment are shown in Fig. 3(a). Both curves can be well described by mono-exponential decays, from which coherence times of $T_2 = 50 \pm 0.5$ ps for sample I and $33 \pm 0.5$ ps for sample II can be extracted. These correspond to homogeneous linewidths $\gamma_{D^0X_A} = \hbar/T_2 = 13 - 19$ meV, respectively. We emphasize that these values are more than two orders of magnitude smaller than the inhomogeneous widths of the optical transitions ($\sim 1$ meV). The small difference in decoherence rates in the two samples can originate from different levels of impurities and defects. Nevertheless, the small homogeneous widths of the D$^0$X$_A$ optical transitions indicate a high crystal quality.

Figure 3(b) demonstrates the SPE decays measured at $\tau_{12} = 6.67$ ps and 13.3 ps for samples I and II, respectively. The extracted decay times are $T_1 = 30 \pm 0.5$ ps for sample I and $T_1 = 39 \pm 1$ ps for sample II. Sample II exhibits additionally a long-lived component with $T_1 = 39$ ps and $T_1 = 1$ ns, respectively. The extracted decay times are given in panels.

FIG. 3. (Color) PE and SPE amplitude decays measured at $T = 1.8$ K as function of delays $\tau_{12}$ and $\tau_{23}$, respectively. (a) PE decays and (b) SPE decays measured for D$^0$X$_A$ in samples I and II. (c) PE decay and (d) SPE decay measured from D$^0$X$_B$ (3.3627 eV) in sample I. $\tau_{12}$ delays used and decay times extracted from exponential fits are given in panels.

Next, we compare the coherence of D$^0$X$_A$ and D$^0$X$_B$ in sample I. Figures 3(c) and 3(d) show the PE and SPE decays at the D$^0$X$_B$ optical transition, respectively. From exponential fits we evaluate a coherence time of $T_2 = 3.6$ ps and a population decay time $T_1 \approx 22$ ps for D$^0$X$_B$. Thus, the homogeneous linewidth of the optical transition, $\gamma_{D^0X_B} = 180$ meV, is about an order of magnitude larger than $\gamma_{D^0X_A}$. The fast decoherence of D$^0$X$_B$ cannot be attributed to energy relaxation because the population decay remains approximately the same as for D$^0$X$_A$. Therefore, in contrast to D$^0$X$_A$, pure dephasing dominates for D$^0$X$_B$. This is a surprising result because the A and B donor bound excitons have similar binding energies and, therefore, occupy the same localization volume. A possible explanation for this unexpected behavior is that the D$^0$X$_B$ states are located in close proximity to D$^0$X$_A$ excited states [24]. Coupling of these states could explain the faster loss of coherence of D$^0$X$_B$.

Finally, to get deeper insight into the coherence properties of donor-bound excitons, we study the PE decay camera on the same sample [18] and the $\tau_0 \approx 160$ ps for a similar ZnO epilayer [19]. This difference indicates that the SPE decay time $T_1$ observed here is limited not only by the exciton lifetime, but also by other energy relaxation processes, to which the photoluminescence is insensitive. The relaxation mechanisms behind this exciton decay shortening require further studies.
rate in sample I as function of temperature and optical excitation intensity. The temperature dependences of coherence and population decay times measured on D⁰Xₐ are shown in Fig. 4(a). While T₁ is temperature independent up to 12 K, the coherence time decreases as ~ 1/T in accord with the linear increase of the acoustic phonon population leading to pure dephasing of the excitons. As already mentioned before, at T = 1.8 K, T₂ ≈ 2T₁ indicating that additional irreversible dephasing mechanisms are negligible. It is also striking that both times, T₂ and T₁, are independent of optical excitation intensity as demonstrated in Figure 4(b) for variation of the first pulse intensity over almost one order of magnitude. We also checked that these times remain the same even when the second and third pulse powers are increased up to several mW.

Conclusions. Epitaxial ZnO layers were studied using coherent optical spectroscopy. Two-pulse and three-pulse photon echoes were observed from the donor-bound A and B excitons. D⁰Xₐ shows a coherent dynamics on timescales of several tenths of picoseconds, corresponding to a homogeneous linewidth of 13-19 µeV at T = 1.8 K. That the D⁰Xₐ coherence time is independent of excitation intensity supports the hypothesis that these excitons can be coherently driven in a robust manner by the optical field. On the contrary, the D⁰Xₐ dephasing is much faster than that for D⁰Xₐ (T₂ = 3.6 ps and 50 ps, respectively), whereas the population decay times are comparable (T₁ = 33 ps for D⁰Xₐ and 22 ps for D⁰Xₐ). This indicates that pure dephasing dominates for D⁰Xₐ, in contrast to D⁰Xₐ. We also show that acoustic phonons play important role, limiting the donor-bound exciton coherence in ZnO at elevated temperatures. In comparison with other wide-bandgap wurtzite semiconductors, CdS was reported to show a coherence time of 800 ps, comparable with its lifetime of 1000 ps, for the neutral acceptor-bound exciton [23]. Due to the much larger oscillator strength, the coherent optical dynamics of the donor-bound exciton in ZnO is significantly shorter lived, making ZnO an attractive candidate for fast coherent control as compared to other wide-bandgap semiconductors.

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