

Nonequilibrium carrier dynamics in MOVPE–grown homoepitaxial ZnTe layers and substrate material

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Introduction

High efficiency light emitting diodes (LEDs) and laser diodes (LDs) operating in the green spectral region (520–580 nm) are needed as light sources in TV projectors and for signal transmissions (at around 560 nm) through polymer optical fibres. Very recently, studies in the field have focused on ZnTe and its alloys to achieve the fabrication of such devices. This is because ZnTe has a RT energy gap of 2.26 eV (548.5 nm). One advantage of this material over the usual GaP–based green–yellow LEDs is its direct energy–gap, which guarantees the fabrication of bright light emitting devices. Recently, high structural quality large (up to 3" in dia.) ZnTe single crystals grown by the vertical gradient freezing (VGF) method became available [1,2]. These crystals are easily p–type doped by phosphorous to achieve net hole concentrations in the 10^{17} – 10^{18} cm^{–3} range. The possibility of realising a vertical p–i–n diode by using these highly conductive p–type ZnTe substrates brings a distinct fabrication advantage over conventional III–N based devices on highly insulating sapphire, the latter requiring complex design and processing steps to provide lateral electrical contacting of the device. This has stimulated attempts to fabricate LEDs structures on ZnTe substrates by both molecular beam epitaxy [3] and metalorganic vapour phase epitaxy (MOVPE).

In this paper we report on the study of sub–nanosecond carrier dynamics in both MOVPE–grown homoepitaxial ZnTe epilayers and VGF–grown substrate crystals using the non–degenerate four wave mixing (FWM) technique, combined with a picosecond optical parametric oscillator.

Experimental

ZnTe epilayers were grown by atmospheric pressure MOVPE on (100)ZnTe:P wafers. Phosphorus concentration in the ZnTe:P wafers ranged between 7×10^{17} and 1.5×10^{18} cm^{–3}. ZnTe epilayers were grown using electronic grade dimethylzinc [DMZn] and di–isopropyl–telluride [DIPTe], as Zn and Te precursors [4]. All samples were grown under a [DIPTe]/[DMZn] stoichiometry ratio in the vapour phase around 1.0, on ZnTe substrates in–situ H₂ annealed at 350 °C, as these conditions have proved to give epitaxial layers with optimised structural, morphological and optical properties. More details on the growth procedures and physico–chemical characteristics of the materials are reported in refs. [4,5].

FWM measurements were performed at room temperature on three 3 μm thick ZnTe homoepitaxial layers grown at 325°C, 350°C and 375°C, varying both the grating period and the excitation wavelength and intensity. The photoelectric properties of the layers were compared with those of the as–received VGF–grown ZnTe:P and undoped wafers (the latter with resistivity 1×10^3 Ohm x cm).

The non–equilibrium carrier gratings were formed in the samples by two interfering 25 ps pulses, produced by an optical parametric oscillator (OPO) [6]. For measurements of the epilayer carrier dynamics we used excitation wavelengths in the range 530–470 nm, strongly absorbed in ZnTe. Therefore, only a thin surface region of thickness $d \approx \alpha^{-1} \approx 0.16 \mu\text{m}$ was initially excited. However, due to carrier diffusion the actual portion of

the excited crystal increases with time up to a thickness ~ 1 – $2 \mu\text{m}$. Such a regime of “surface” grating allowed us to selectively measure the carrier kinetics in the epilayers. The bulk crystals were instead investigated both with the 500 and 566 nm wavelengths, allowing to excite either a surface region of the wafer or the whole crystal. The excitation intensity in all experiments was varied between 0.25 and 1 mJ/cm². The grating decay was monitored by a third (probe) pulse at 1064 nm wavelength, which was delayed up to 1 ns with respect to the recording (pump)

beams. Silicon photodetectors were used to measure the diffraction efficiency $\eta = I_D/I_T$ (where I_D and I_T are the intensities of the diffracted and transmitted parts of the probe beam). The grating period $\Lambda = \lambda / \sin(\Theta)$ was varied by changing the angle Θ between the recording pump beams.

Results and discussion

In Fig. 1 we compare the kinetics of “surface” gratings for P–doped (a) and undoped (b) (100)ZnTe wafers at four excitation levels. The grating kinetics in these samples exhibits a different dependence on excitation. The grating decay in the undoped ZnTe wafer (Fig.1 b) is single–exponential and relatively fast for all excitation energies, the grating decay times τ_g ranging around 120–160 ps. The grating decay in the P–doped ZnTe also exhibits a similar fast decay ($\tau_g=170$ ps) at the lowest excitation intensity, but for higher excitation the decay becomes slower (τ_g increases up to 690 ps at 1 mJ/cm^2). Such a carrier relaxation behaviour can be ascribed to the electrical activity of some type of defects in the crystal, which act as carrier trapping centres [7]. Apparently the defect concentration in the undoped wafer is higher than that in the P–doped one, as in the latter the trapping centres can be nearly saturated by a pump beam intensity around 1 mJ/cm^2 . Compensation of native defects could be indirectly related to this finding, through the proposed formation of a deep center by excess phosphorus in VGF–grown ZnTe:P [8].

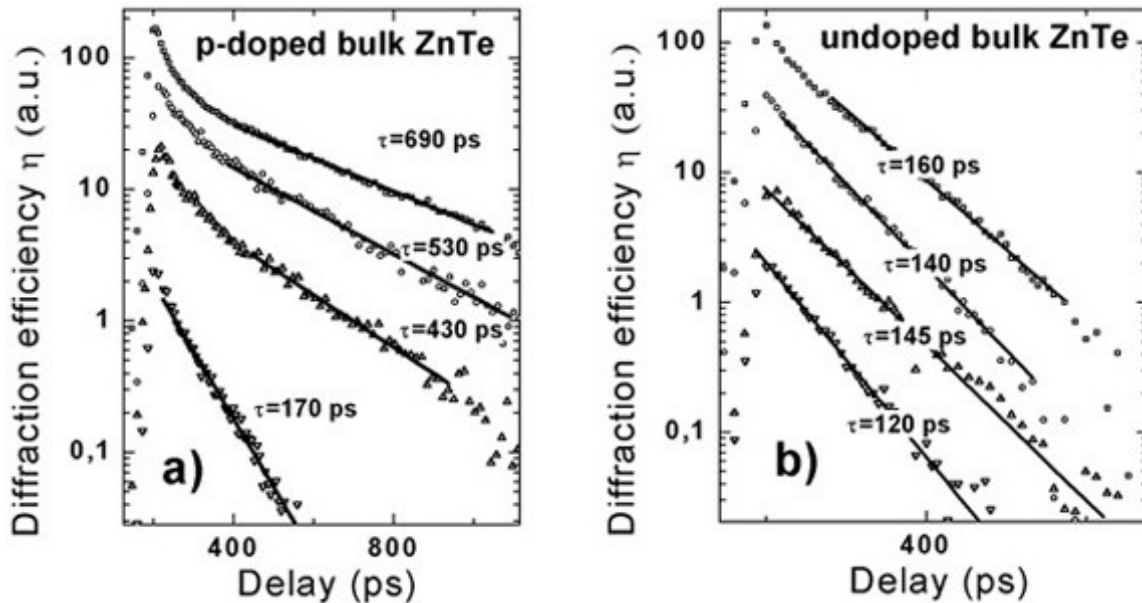


Fig.1 Free carrier grating kinetics in P–doped (a) and undoped (b) bulk ZnTe crystals at four excitation levels, i.e. 0.12, 0.24, 0.53 and 1 mJ/cm^2 . Grating spacing $\Lambda = 11\mu\text{m}$, excitation wavelength $\lambda = 500\text{nm}$

We also measured the grating kinetics in the volume of the ZnTe:P wafer, using excitation at 566 nm, thus creating non–equilibrium carriers with densities in the 10^{16} cm^{-3} range. At all excitation intensities, the grating decay was exponential with τ_g in the 600–700 ps interval. Thus, contrary to the ‘surface’ grating case, we have not observed any fast carrier trapping. In the latter conditions, with a considerably smaller concentration of free carriers (with respect to the surface excitation), the grating decay should have exhibited a fast carrier trapping if a high density of homogeneously distributed defects was present in the crystal. Instead, the different grating decays observed within a few micron depth from the surface and in the volume of the ZnTe:P wafer can be explained assuming that the defect density is higher in the near–surface region of the wafer, while the rest of the crystal remains almost free of these defects, giving rise to relatively longer decays.

Measurements of the grating kinetics in P–doped ZnTe were also performed varying the grating spacing Λ in the

5–12 μm range, allowing us to discriminate between carrier recombination and diffusion processes and to determine the carrier diffusion coefficient D according to the well-known relationship:

$$1 / \tau_g = 1 / \tau_R + 4\pi^2 D / \Lambda^2$$

Measurements at 500 nm ('surface' excitation) and 566 nm (bulk excitation) provided quite similar D values: that is, $D=11.1 \text{ cm}^2/\text{s}$ and $D=11.4 \text{ cm}^2/\text{s}$, correspondingly. In the case of above band-gap excitation, when electrons and holes are generated with equal densities and exceeds the doping concentration, pure bipolar diffusion is expected with D value of about $3 \text{ cm}^2/\text{s}$ [9]. However, the as-determined D values above are much higher than the bipolar value and support instead the assumption of fast electron trapping in the surface region. The D value obtained for bulk excitation, i.e. for non-equilibrium carrier densities less than the hole density in our P-doped ZnTe wafers, corresponds to minority carrier (electron) diffusion coefficient with an electron mobility of about $450 \text{ cm}^2/\text{Vs}$.

The peculiarities of carrier relaxation and transport in the substrates were then compared with the grating decay in the MOVPE-grown epilayers. We excited the front- (epilayer) and back-side (P-doped substrate) of each sample using different wavelengths (Fig. 2a). Whilst, at 566 nm both the epilayer and substrate are excited and the grating decay kinetics correspond to the integrated signal from the whole sample, at shorter wavelengths the excitation depth decreases due to higher absorption coefficients and the FWM signal is generated only within the epilayer or in a thin surface region of the substrate. At the same time the influence of surface recombination increases. Thus, the surface quality of epilayer and substrate can be examined and compared. In this respect, similar shapes of the epilayer and substrate decay curves shown in Fig. 2a indicate that carrier relaxation at the very surface of the crystals is determined by the same 'surface' recombination rate, while the processes at later times are slightly different. Moreover, the decay kinetics measured at 500 nm in the epilayers grown at 325 °C, 350 °C and 375 °C are almost the same, indicating that carrier recombination rate does not critically depend on epilayer growth temperature.

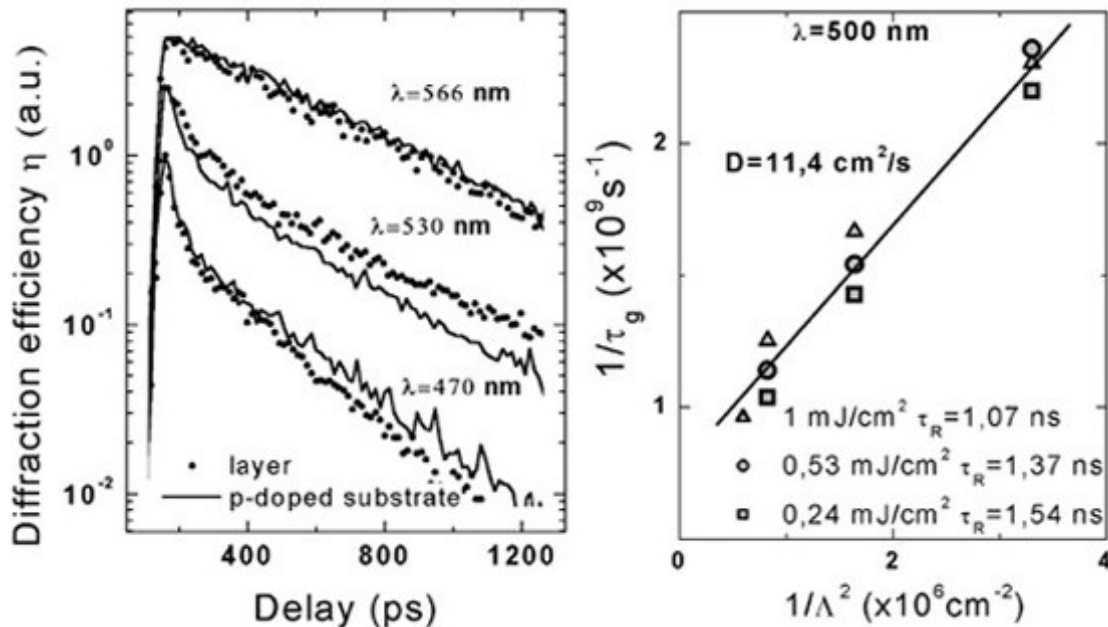


Fig.2 (a) Free carrier grating kinetics in the P-doped substrate and in the 350 °C grown epilayer, for three excitation wavelengths; **(b)** dependence of the grating decay time τ_g on the grating period Λ for the 350°C epilayer provides values of diffusion coefficient D and carrier lifetime τ_R at the given excitation energy

It is worth to note that studies at various excitation energies of carrier transport and recombination in the epilayers (Fig. 2b) indicated one essential feature: a decrease of carrier lifetime τ_R with excitation intensity (from ~ 1.5 ns at 0.24 mJ/cm² to ~ 1 ns at 1.07 mJ/cm²), i.e. contrary to what found for the P-doped substrate surface, where an increase of carrier lifetime was found (Fig. 1a). This tendency, together with the ns-long lifetimes showed by the epilayers can be clearly ascribed to a dominant bimolecular carrier recombination and a low density of trapping defects in the epilayers. Instead, the high value of D found for the epilayer is very close to one of the P-doped ZnTe substrate, pointing out towards the occurrence of similar levels ($\sim 10^{18}$ cm⁻³) of ionised impurities in both epitaxial and bulk crystals, despite the high optical quality demonstrated by our MOVPE material [4,5]. Hall measurements performed on homoepitaxial samples grown on undoped ZnTe substrates under similar conditions show however, that the epilayers have RT net hole concentrations $p \sim 10^{16}$ cm⁻³. This suggests that the MOVPE-grown material must be fairly compensated; this is in qualitative agreement with the results of a preliminary analysis of Hall data, leading to values of the compensation ratio $K = N_D/N_A$ in the 0.96–0.99 interval [10]. Moreover, secondary ion mass spectrometry in-depth elemental analysis of as-grown samples showed that P diffusion from the substrate can be ruled out. Thus, the origin of such high compensation and the nature of impurities involved is not yet clear at the moment and it will require further studies.

Conclusions

We characterised the RT photoelectric properties of MOVPE-grown homoepitaxial ZnTe layers and of both P-doped and undoped VGF-grown ZnTe wafers by degenerate FWM technique, using an optical parametric oscillator. Carrier lifetimes and bipolar diffusion coefficients in the epilayers and in the wafers have been compared at different excitation wavelengths. We found strong electrical activity of trapping centres in the undoped wafers, while in P-doped wafers their activity is reduced and can be saturated by strong photo-excitation; this difference could be ascribed either to a lower proclivity of the doped material towards surface mechanical damaging during lapping/polishing procedures of the wafer (impurity hardening) or to the proposed formation of a deep centre by excess phosphorus in VGF-grown ZnTe:P. However, ns-long lifetimes were found in nominally undoped epilayers, ascribable to a dominant bimolecular carrier recombination and a low density of trapping defects. The electron diffusion coefficient in the epilayers turned out to be almost the same ($D = 11.4$ cm²/s) as that of the ZnTe:P wafers, allowing the determination of a RT electron mobility value of 450 cm²/Vs: this pointed out the role of ionised impurities on the electron scattering in present MOVPE-grown material.

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