Investigation of ZnTe homoepitaxial layers grown by metalorganic vapour phase epitaxy on VGF–grown (100)ZnTe:P wafers

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Introduction

High efficiency light emitting diodes (LEDs) and laser diodes operating in the green spectral region (i.e., around 520–580 nm) are needed as novel light sources in TV projectors and for signal transmissions (at around 560 nm) through polymer optical fibres.

Very recently, researches in the field have focused on ZnTe and its alloys (such as ZnCdTe and ZnMgCdTe) 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]. The reported etch pit density of 2'' diameter wafers is around 2000 cm^{-2} . These crystals can be easily made p–type by phosphorous doping 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. Finally, III–N LEDs and LDs operating in the 560 nm region require high indium content alloys, which are difficult to growth using the current high temperature MOVPE process of these compounds.

The potentialities of ZnTe have recently stimulated a technological effort on the fabrication of ZnTe–based LEDs; such devices have indeed been successfully realized by MBE [3,4], whilst not much work has been reported yet in the literature on the MOVPE growth of the same structures. However, the structural and optical properties of homoepitaxial ZnTe and its alloys are still far from being device–quality and need further optimisation.

This work deals with the optimisation of MOVPE growth conditions of nominally undoped ZnTe epilayers on p–type ZnTe:P substrates and their subsequent structural, morphological and optical characterisation.

Experimental

ZnTe epilayers were deposited on VGF–grown (100)ZnTe:P wafers by atmospheric pressure MOVPE in an home–made horizontal vent–run reactor. Substrates with hole concentrations ranging between $7x10^{17}$ cm^{-3} and $1.5x10^{18}cm^{-3}$ and etch–pit densities below $3x10^{4}$ cm^{-2} were supplied by Nikko Materials Co. Ltd (Japan). As there appeared some damage left on the wafer surface by the lapping/polishing treatments performed on the wafers after cutting from the ingot, these were etched at RT for 2 minutes in a 1% Br_2–methanol solution to remove the first few microns of material. Before being loaded into the reactor, the wafers were subsequently treated for 30 seconds in a 3% HF–deionised water solution [5], as this improves the initial nucleation and structural quality of the over–grown ZnTe epilayer by smoothing the wafer surface and removing residual contamination. An in–situ thermal treatment under 1.0 slm H_2 flow was then applied for 10 min immediately prior to the growth to remove any trace of oxides from the surface; the temperature of the treatment (T_a) was varied between 190 °C and 350 °C to determine best thermal conditions for this process. Electronic grade dimethylzinc (Me_2Zn) and di–isopropil–telluride (^{i} PrTe) supplied by Ephichem, Ltd. were used as Zn and Te precursors respectively. All samples were grown under a total H_2 carrier flow of 4.55 sl/min and molar flows of 53 mmol/min and 55 mmol/min for the Zn and Te alkyls, respectively. The sample growth temperature (T_g) and the substrate in–situ annealing temperature (T_a) were investigated separately in this work by varying first Ta within the stated interval, whilst keeping fixed T_g at 340°C; then T_g was changed between 325°C and 400°C with Ta fixed at 350°C. The

thickness of the epilayers was varied between 0.35 and 3 μm.
Field emission gun scanning electron microscopy (SEM–FEG) observations were performed on the epilayers to investigate their surface morphology, for this purpose a Jeol model JSM 6500 F was used with a primary electron beam energy of 5 kV. In order to detect impurities incorporated in the layers during the growth, secondary ion mass spectrometry (SIMS) measurements were employed. Elemental depth profiles of ^{19}F, ^{23}Na, ^{27}Al, ^{35}Cl, ^{63}Cu were obtained by a Cameca IMS 4F instrument by the use of 14.5 keV Cs^+ primary ion beam and detecting secondary negative ions. The Cs^+ primary beam current was 50 nA. To investigate the crystalline structure of as–grown ZnTe epilayers, high resolution X–ray diffraction (HRXRD) measurements close to the symmetric (004) reciprocal lattice points were executed by using a diffractometer Philips model MRD, equipped with a four crystal channel–cut monochromator. Finally, photoluminescence (PL) measurements were performed at 4.2 K to check the optical quality of the ZnTe samples. PL measurements were relised by exciting the sample with the 325 nm line of a He–Cd laser with an excitation intensity of 70 mWatt/cm^2 whilst a halogen lamp was used for the REFL measurements.

Results and discussion

HRXRD close to the symmetric (400) and asymmetric (115) reciprocal lattice points revealed that for all samples the ZnTe epilayer is pseudomorphic with respect to the ZnTe substrate. Fig. 1 reports the rocking curves measured in the vicinity of the ZnTe (400) reflection of samples grown at T_g =350°C and whose substrates were annealed at different temperatures T_a and, for comparison, that of the substrate.

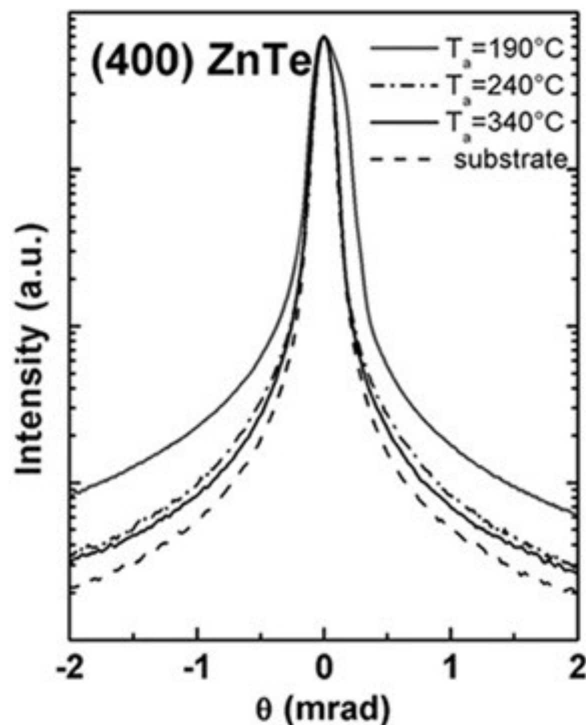

Fig 1: (400) HRXRD of 350 nm thick ZnTe epilayers grown with three different pre-growth annealing temperatures and of ZnTe:P substrate

It appears that epilayers grown on substrates annealed at T_a >=240 °C exhibit a good crystalline quality, as evidenced by the 140 μrad value of the peak FWHM , i.e. comparable to that of the substrate. On the contrary, substrate annealing at T_a =190 °C lead to a sample with a larger (190 μrad) FWHM value. This result strictly correlates to what previously evidenced by the SIMS depth analysis of the oxygen content at the epilayer/substrate interface [5]: it was there concluded that annealing under H_2 at temperatures above about 240 °C were necessary to reduce most (although probably not all) of the native oxides left on the wafer surface after chemical etching.
Present HRXRD data show that, although the long range perfection of the crystal doesn't improve by increasing T_a above 240 °C, the (400) peak diffused X–ray scattering (i.e., the height of the rocking curve tails around the peak) still continues to reduce monotonically when T_a is increased from 240°C to 340°C, indicating that the microscopic quality of the epilayer improves by increasing the wafer annealing temperature up to 350 °C. For this reason, all subsequent growth experiments were performed at T_a =350 °C.
Several samples were thus grown varying the material growth temperature T_g . Both HRXRD measurements and SEM–FEG observations have shown that the structural quality and morphology of the epilayers strongly depend on Tg. Fig. 2 reports the SEM–FEG micrographs of 3 μm thick samples grown at different temperatures (see Figure): it clearly appears that the best surface morphology is obtained for the epilayer grown at 350°C, its surface appearing featureless even at a magnification of 15000x (Fig. 2d). Preliminary HRXRD measurements of these samples have shown that samples grown at 350 °C also show best crystalline quality.

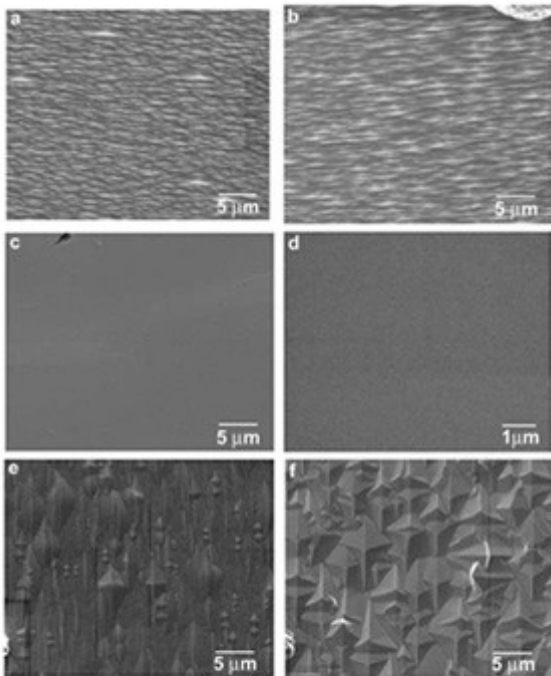

Fig. 2 SEM-FEG micrographs of ZnTe epilayers grown at different temperatures with a VI/II =1 and Ta=350°C, epilayers thickness is 3 µm. For pictures a), b), c), e) f) magnification is 3500x, for picture d) magnification is 15000x.
a) Tg = 325°C, b) Tg = 340°C, c) and d) Tg = 350°C, e) Tg =375°C, f) Tg = 400°C.
It is evident that the best quality morphology is achieved for a growth temperature of 350°C.

PL measurements were performed on the 3 µm thick samples grown at 325 °C, 350 °C, 375°C and 400 °C. The 4.2 K PL spectra of these samples are shown in Fig. 3b. The main features of the PL emissions confirm what described in a previous paper [5]. In fact, all samples show a band–edge emission in the region between 2.370 eV and 2.395 eV, followed by two large bands: one peaked at 2.363 eV, ascribable to a free–to–bound (FB) transition; the second at 2.330 eV, followed by its LO phonon replica at lower energy: this latter band is due to a donor–acceptor pair (DAP) recombination. The best optical quality is obtained for the samples grown at 350 °C, showing a dominant narrow free exciton emission (X_{1s}). Noteworthy, this emission completely disappears at T_g =325 °C, while it monotonously weakens for growth temperatures above 350 °C. Fig 3a shows the band edge PL spectrum of the sample grown at 350°C along with the reflectivity spectrum. This demonstrates that the X_{1s} peak at 3.3809 eV can indeed be ascribed to the 1s–state free exciton emission, its FWHM being 1.65 meV. In the band edge spectrum, the weaker emission lines at lower energy, namely at 2.3776 eV, 2.3739 eV and 3.3748 eV can be ascribed to a donor bound exciton (D_1) and to two acceptor bound exciton ($A_1$and A_2) lines, respectively.
According to the literature, the D_1 emission line could be ascribed to Cl [6], whose presence have been detected by SIMS depth profiling analysis on several samples, ascribable to residual halide contaminations in the m.o. sources; weak traces of F were also detected in all samples, possibly due to residual surface contamination after the HF–etch of the wafer prior the deposition. No traces of Na, Al and Cu were instead detected. The origin of the acceptor bound exciton lines remains thus to be understood.

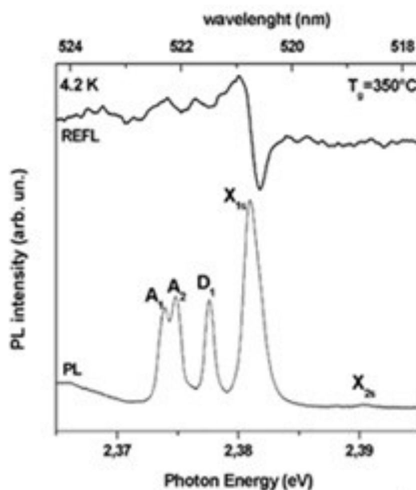

Fig3a 4.2K photoluminescence (PL) and reflectivity (REFL) spectra of a 3 µm ZnTe sample grown at 350°C.

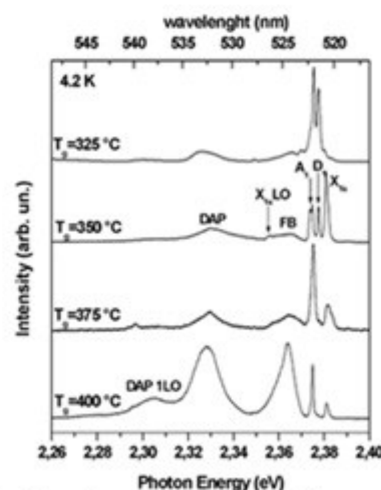

Fig 3b PL spectrum of 3 µm thick samples grown at different temperatures; the excitation wavelength used is 325 nm.The sample grown at 350°C is the only one in which 1s free-exciton emission is dominant, thus revealing a better optical quality.

As far as the origin of the FB and DAP bands is concerned, we previously assigned them to the luminescence of the P–doped substrate, excited by the intense near band edge luminescence of the epilayer [5].

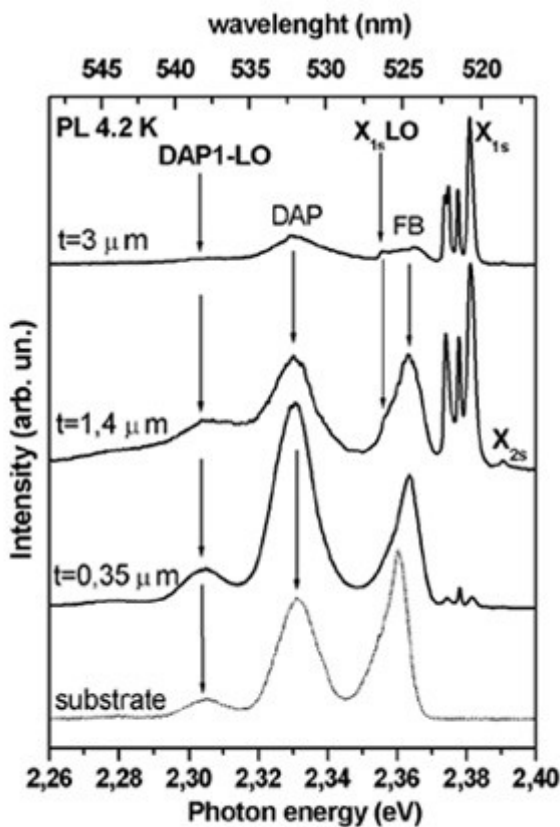

Fig. 4: PL spectra of three ZnTe epilayers grown at 350°C with different thickness (solid line) and PL spectrum of ZnTe:P substrate (dashed line). The excitation wavelength used for the epilayers is 325 nm, the one for the substrate is 441,6 nm.

Indeed, the relative intensities of these two bands to the sample band edge emission decreases by increasing the epilayer thickness, as showed in Fig. 4, further confirming our claim. In the same Figure, the PL spectrum of the substrate is also reported for comparison.

Conclusions

ZnTe epilayers were grown by atmospheric pressure MOVPE on (100) ZnTe:P substrates. The effects of the wafer in–situ annealing temperature T_a and of the epilayer growth temperature T_g on the structural, morphological and optical properties of the material were investigated. This allowed us to determine growth conditions which achieve optimised layer properties.

It was demonstrated that the epilayer crystalline quality strongly improves by increasing the wafer in–situ annealing temperature T_a from 190°C to 240°C, in agreement with a previous SIMS analysis, indicating that annealing temperatures >= 240°C are necessary to reduce most native oxides from the wafer surface. Best (400) peak FWHM around 140 µrad were thus obtained. However, the microstructure of ZnTe epilayers continues to be improved by a further increase of the annealing temperature up to 350 °C, indicating that the wafer annealing also affects the amount of crystal defects generated in the epilayer (most likely close to the epilayer/substrate interface) during the growth. Further analysis are needed to clarify the exact origin and nature of these defects, although, present results points out towards the role of residual oxides at the wafer surface, which seems to be completely removed only after annealing the wafer surface at temperatures well above 240 °C.

Investigations of the epilayer structure and morphology vs. their growth temperatures has shown that best crystalline properties and surface morphology are achieved at a growth temperature of 350°C. In particular, SEM–FEG observations indicated that this temperature provides epilayers with nearly featureless surfaces. Also the optical quality of samples grown at 350°C shows the best properties, with a dominant and intense free exciton emission.

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