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Structural study of (100) CdTe epilayers grown by MOVPE on ZnTe buffered and unbuffered (100) GaAs

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Abstract

We report on the structural assessment of metalorganic vapour phase epitaxy grown (100)-oriented CdTe epilayers on both (100)GaAs and (100)ZnTe/GaAs. Ion channelling Rutherford backscattering spectrometry and cathodoluminescence (CL) measurements are used to study the effect of inserting a proper ZnTe buffer layer [G. Leo et al., *J. Vac. Sci. and Technol. B* 14 (1996) 1739] between CdTe and GaAs. The insertion of a ZnTe buffer layer improves the surface crystalline and optical quality of the CdTe: CL images show that non-radiative recombination regions, associated with extended defects, strongly decrease when a ZnTe buffer layer is used. Also, enhanced excitonic emissions are observed in the case of CdTe/ZnTe/GaAs samples.

1. Introduction

Cadmium telluride is a direct band gap semiconductor ($E_G = 1.5$ eV) which is continuing to attract much technological interest, being an important material for high efficiency solar cells, γ - and X-ray detectors and opto-electronic applications [1–5].

Moreover the good chemical compatibility and close lattice matching with HgCdTe and CdZnTe, make CdTe an ideal substrate for the epitaxial growth of narrow gap II–VI semiconductors for infrared

detector applications. In this respect, the lack of high quality and large area single crystal substrates of CdTe, has stimulated the growth of epitaxial CdTe layers on GaAs as hybrid substrates for the subsequent epitaxy of HgCdTe epilayers. Metalorganic vapour phase epitaxy (MOVPE) [6,7], atomic layer epitaxy (ALE) [8], molecular beam epitaxy (MBE) [9] have been the most used techniques. Nevertheless, CdTe/GaAs heterostructures present a high lattice mismatch (14.6%) which is not entirely relieved at the interface by misfit dislocations: high density of threading dislocations extending through the epilayer are observed, even if this density decreases with the epilayer thickness [10,11]. Besides, epitaxial CdTe on (100)GaAs exhibits a three-dimen-

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sional growth mode and both (111) and (100) CdTe oriented layers can be obtained depending on the conditions of annealing temperature, surface reconstruction and stoichiometry of the GaAs substrate [12–16].

In order to intentionally nucleate the CdTe layer along the (100) direction as well as to reduce the large CdTe/GaAs mismatch, the insertion of a ZnTe buffer layer has been sometimes reported in the literature [16,17]. However, to our knowledge, only a few studies of the CdTe structural quality grown on a ZnTe buffer layer have been published [18].

In a previous paper [19], we reported on the structural characterisation of MOVPE-grown (100) CdTe epilayers as a function of the thickness of a ZnTe buffer layer deposited on GaAs. It was evident from both Rutherford backscattering spectrometry (RBS) channelling and double crystal X-ray diffractometry (DC-XRD) measurements that the insertion of a ZnTe buffer layer causes a noteworthy improvement in the structural quality of the CdTe epilayers. Single-crystal (100)CdTe epilayers of fairly good crystalline quality were obtained for ZnTe buffer layer thicknesses in the range from 300 to 500 nm.

In this work we further report on the cathodoluminescence (CL) and RBS channelling characterisation of CdTe epilayers grown on optimised ZnTe buffer layers deposited on (100)GaAs. A study of the CdTe surface defect density is presented and compared to what is obtained for CdTe epilayers grown directly on (100) GaAs.

2. Experimental procedure

CdTe epilayers were grown on (100)GaAs substrates by atmospheric pressure metalorganic vapour phase epitaxy (MOVPE) in a horizontal chamber reactor of the vent–run type. For most samples a 300 nm thick ZnTe buffer layer was grown on GaAs before depositing CdTe. To this purpose electronic grade dimethyl-cadmium (Me_2Cd), di-isopropyltelluride ($(i\text{-Pr})_2\text{Te}$) and dimethyl-zinc (Me_2Zn), supplied by Epichem, Ltd. were used as Cd, Te and Zn precursors, respectively.

GaAs substrates cut from LEC-grown semi-insulating (resistivity $> 10^7 \Omega \cdot \text{cm}$) $(100) \pm 0.25^\circ$ oriented 2" wafers, were supplied by Japan Energy,

Ltd. Before being loaded into the reactor, the substrates were degreased in iso-propanol vapour and then etched for 8 min at 40°C in a $\text{H}_2\text{SO}_4 : \text{H}_2\text{O}_2 : \text{H}_2\text{O}$ (4:1:2) solution, rinsed in 18.2 M Ω deionized water and finally dried under pure N_2 flow. In order to get an oxide-free surface an in situ thermal treatment was routinely performed on the GaAs substrates at 460°C for 20 min under 1.0 slm total H_2 flow immediately before the growth. For all samples the growth temperature was kept fixed at 350°C , whereas the molar flows of Me_2Cd , $(i\text{-Pr})_2\text{Te}$ and Me_2Zn through the reactor chamber were fixed at about $55 \mu\text{mol}/\text{min}$, achieving a precursor concentration of about $1.2 \times 10^{-8} \text{ mol}/\text{cm}^3$ in the vapour phase for a total H_2 dilution flow of about 4.5 slm. These conditions gave us growth rates of about $2.1 \mu\text{m}/\text{h}$ for ZnTe and $2.5 \mu\text{m}/\text{h}$ for CdTe. Furthermore, in order to have sharp CdTe/ZnTe interfaces, a 60 s growth interruption time was adopted between the growth of ZnTe and CdTe. Several CdTe epilayers were grown for the present study, their thicknesses ranging from 200 to 1100 nm, while the ZnTe buffer layer thickness was fixed at the optimised thickness of 300 nm [19].

Cathodoluminescence measurements were performed on a Cambridge Stereoscan 350 scanning electron microscope fitted with an Oxford Instruments Mono-CL system at the CNR-MASPEC laboratory in Parma. Analysis were carried out both at room temperature and at liquid nitrogen temperature, the electron beam energy being varied between 10 and 20 keV.

In order to measure the epilayer thickness and to estimate their crystalline quality, Rutherford backscattering spectrometry (RBS) measurements in both random and [100] aligned geometry (ion channelling) were performed at the Laboratori Nazionali di Legnaro (Italy) on both CdTe/GaAs and CdTe/ZnTe/GaAs heterostructures by using $^4\text{He}^+$ beams of 2 or 3.5 MeV energy, depending on the thickness of the structure.

3. Results and discussion

Fig. 1 shows the behaviour of χ_{min} , i.e. the RBS channelling yield normalised to the random yield at the CdTe/ZnTe/GaAs heterostructure surface, as a

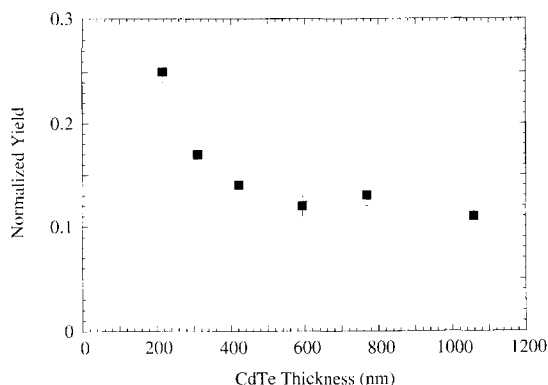


Fig. 1. Values of the [100]-aligned RBS minimum yield, χ_{\min} , as a function of the CdTe epilayer thickness, the ZnTe buffer layer thickness being 307 nm.

function of the thickness of the CdTe layers. Bearing in mind that the lower the value of χ_{\min} , the better the crystalline quality of the sample near the surface, the data in Fig. 1 show that the surface quality of the CdTe epilayers strongly improves as the thickness increases up to 400 nm, above which χ_{\min} saturates at about 12%. Notably, this saturation value is almost four times lower than the one ($\chi_{\min} \approx 44\%$) obtained without the insertion of the ZnTe buffer layer for the same CdTe thickness.

The high χ_{\min} values measured below 400 nm have been previously ascribed to the presence of extended defects arising from the CdTe/ZnTe lattice misfit relaxation [19]. In fact, strain measurements by ion channelling show that the compressive strain due to the lattice mismatch between CdTe and ZnTe is already relaxed at the top of a 300 nm thick CdTe epilayer, although a small residual thermal strain ($\epsilon_{\parallel} = -0.02\%$) is measured at the surface of the CdTe/ZnTe/GaAs heterostructure, due to the variation of the lattice parameters between the growth temperature and room temperature. Moreover, for thicker CdTe layers, χ_{\min} saturates at 12% which is about twice the value obtained in a defect-free crystal of CdTe [20]. This deviation points out that the extended defects propagate well beyond the region where much of the strain is released, reaching the surface of the epilayer even in samples as thick as 1 μm or more.

The above results are confirmed by DC-XRD measurements [19]. In fact the full width half maxi-

um (FWHM) of the (400) peak of a 435 nm thick CdTe layer decreases from 1575 to 1088 arcsec as a consequence of the insertion of the optimised ZnTe buffer layer between the CdTe and the GaAs substrate. By increasing the thickness of the CdTe layer to 1 μm , the FWHM further decreases only slightly to about 900 arcsec, which is still well above the value of 42 arcsec expected for a perfect crystal of CdTe having the same thickness. In this respect, it should be considered that DC-XRD only gives an assessment of the average crystal quality of the whole CdTe epilayer including the highly defected region near the interface.

A direct image of the crystalline quality of the near-surface region of the CdTe layer is obtained by cathodoluminescence. Two samples with a 1 μm thick CdTe top layer were analysed, one with the optimised 300 nm thick ZnTe buffer layer inserted between the CdTe film and the GaAs substrate and the other without any buffer layer. Fig. 2a and Fig. 2b show the panchromatic CL images of the two samples at room temperature. Almost all the dark dots shown in the micrographs are caused by the enhanced non-radiative recombination at extended defects, namely threading dislocations propagating from the near interface region to the epilayer surface. This is confirmed by the observation of the dark spots at different beam energies (from a few to 20 keV), their CL contrast increasing with temperature as found by Watson and Durose in bulk CdTe crystals [21].

It is quite evident that the density of dark dots is by far higher in the CdTe/GaAs sample (Fig. 2a) compared with the CdTe/ZnTe/GaAs heterostructure (Fig. 2b). The effect of the ZnTe buffer layer is to reduce the density of dark dots down to about 10^7 cm^{-2} , although the actual density of threading dislocations may be larger since the average size of the dark dots is comparable to the limiting spatial resolution of the CL technique.

These results explain the dramatic improvement of the near-surface quality of the CdTe films observed by RBS channelling. Finally, the optical quality of the two samples is compared in Fig. 2c, where the CL spectra of the CdTe/GaAs and the CdTe/ZnTe/GaAs samples are shown. The spectra were collected at liquid nitrogen temperature and low magnification. Both the spectra exhibit the exci-

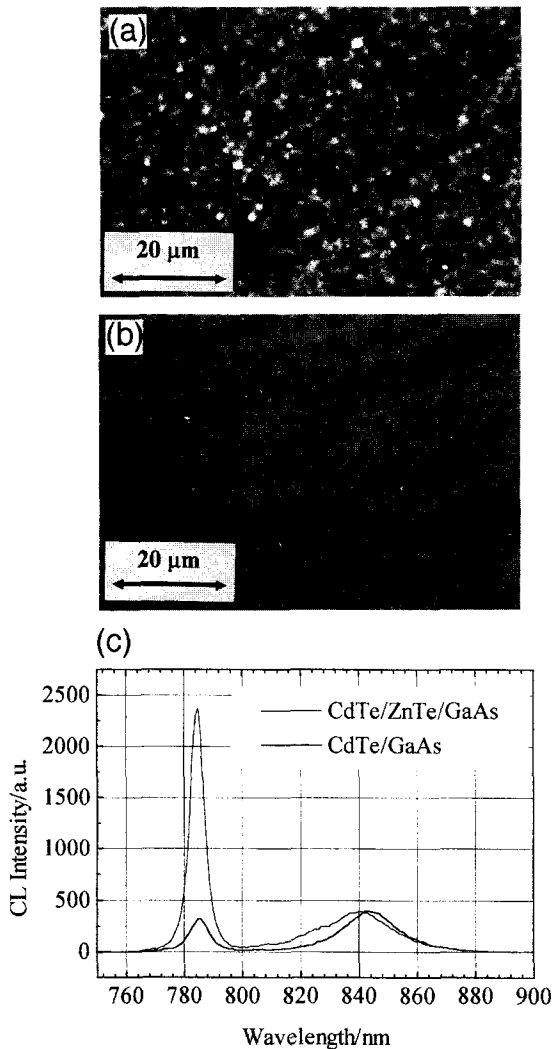


Fig. 2. Room temperature panchromatic CL image of a CdTe layer grown on (a) GaAs and (b) ZnTe/GaAs. The thicknesses of the CdTe and ZnTe layers are 1 μm and 307 nm, respectively. (c) 77 K CL spectra of samples with the buffer layer (grey line) and without the buffer layer (black line).

ton peak at 1.58 eV, although its intensity is higher for the CdTe/ZnTe/GaAs sample with respect to the CdTe/GaAs heterostructure. This indicates that the optical and structural quality of the buffered sample is much better. Finally, a broad emission band appears in both samples around 1.47 eV. Such a band is related to impurities, most of which tend to gather around the extended defects.

4. Conclusions

We have studied the crystal quality at the surface of (100) CdTe epitaxial layers grown on (100) GaAs substrates. The reduction of the density of threading dislocations at the surface by the insertion of a ZnTe buffer layer of suitable thickness (300 nm) between the film and the substrate is shown by cathodoluminescence. The ZnTe buffer layer causes a strong improvement of the structural and optical quality of CdTe layers at the surface as confirmed also by RBS channelling and supports the usefulness of a ZnTe buffer layer in growing good quality epitaxial (100) CdTe on (100) GaAs.

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References

- [1] C. Scheiber and J. Chambran, Nucl. Instrum. Methods Phys. Res. A 322 (1994) 604.
- [2] J. Britt and C. Ferekides, Appl. Phys. Lett. 62 (1993) 2851.
- [3] R.K. Ahrenkil, B.M. Keyes, D.L. Levi, K. Emery, T.L. Chu and S. Chu, Appl. Phys. Lett. 64 (1994) 2879.
- [4] M. Fiederle, D. Ebling, C. Eiche, D.M. Hofman, M. Salk, W. Stadler, K.W. Benz and B.K. Meyer, J. Crystal Growth 138 (1994) 529.
- [5] A. Nouhi, R.J. Stirn, P.V. Meyers and C.H. Liu, J. Vac. Sci. Technol. A 7 (1989) 833.
- [6] I. Bhat and W.S. Wang, Appl. Phys. Lett. 64 (1994) 566.
- [7] P.L. Anderson, J. Vac. Sci. Technol. A 4 (1986) 2162.
- [8] W.S. Wang, H.E. Ehsani and I.B. Bhat, J. Crystal Growth 124 (1992) 670.
- [9] J.P. Faurie, R. Sporcken, Y.P. Chen, M.D. Lange and S. Sivanathan, Mater. Sci. Eng. B 16 (1993) 51.
- [10] K. Durose and H. Tatsuoka, Inst. Phys. Conf. Ser. 134 (1993) 581.
- [11] H. Tatsuoka, H. Kuwabara, Y. Nakanishi and H. Fujiyasu, J. Crystal Growth 117 (1992) 554.
- [12] S. Sone, M. Ekawa, K. Yasuda, Y. Sugiura, M. Saji and A. Tanaka, Appl. Phys. Lett. 56 (1990) 539.
- [13] A. Bourret, P. Fuoss, G. Feuillet and S. Taterenko, Phys. Rev. Lett. 70 (1993) 311.
- [14] G. Bratina, L. Sorba, A. Antonini, G. Ceccone, R. Nicolini,

- G. Biasiol, A. Franciosi, J.E. Angelo and W.W. Gerberich, *Phys. Rev. B* 48 (1993) 8899, and references therein.
- [15] T.T. Cheng, M. Aindow, I.P. Lones, J.E. Hails, D.J. Williams and M.G. Astels, *J. Crystal Growth* 135 (1994) 409.
- [16] J.W. Cairns, D.A. Woolf, M.R. Bennett, R.H. Williams and R.A. Ballingall, *J. Vac. Sci. Technol. B* 12 (1994) 2587.
- [17] G. Patriarche, R. Triboulet, Y. Marfaing and J. Castaing, *J. Crystal Growth* 129 (1993) 375.
- [18] S.J.C. Irvine, J. Bajaj and H.O. Sankur, *J. Crystal Growth* 124 (1992) 654.
- [19] G. Leo, M. Longo, N. Lovergine, A.M. Mancini, L. Vasanelli, A.V. Drigo, F. Romanato, T. Peluso and L. Tapfer, *J. Vac. Sci. Technol. B* 14 (1996) 1739.
- [20] G. Leo, A. Traverse, M.O. Ruault and A.V. Drigo, *Nucl. Instrum. Methods B* 63 (1992) 41.
- [21] C.C.R. Watson and K. Durose, *J. Crystal Growth* 126 (1993) 325.