Optical and structural studies of Hg$_{0.7}$Cd$_{0.3}$Te samples grown by various methods

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Abstract. Photoluminescence and X-ray diffraction (XRD) were used for the studies of the properties of HgCdTe samples with CdTe molar fraction $x=0.3$ grown by various methods. According to the results of photoluminescence studies, all samples possessed a considerable degree of alloy disorder, yet the scale of the disorder seemed not to be directly related to the structural quality of the material as revealed using XRD. Prospects of using HgCdTe material grown by various methods in optoelectronic devices are discussed.

1. Introduction

Hg$_{1-x}$Cd$_x$Te (MCT) solid solutions are important materials for devices operating in the infrared (IR) part of the spectrum. MCT with CdTe molar fraction (chemical composition) $x=0.3$ are of special demand, as the bandgap $E_g$ of the material ($\sim 270$ meV at the temperature $T=77$ K for $x=0.30$) corresponds to the energy of photons in the middle-wavelength (3-5 $\mu$m) IR (MWIR) range. This spectral range is associated with the fundamental rotational and vibrational resonances of a large number of technologically important molecules, which is important for applications in environmental control, security, defence, energy auditing/conservation, medicine, agriculture, etc. [1].

MCT is widely used in fabrication of photodetectors [2], though attempts to fabricate economically viable MCT-based light emitters also continue [1]. The methods currently used for MCT growth include molecular-beam epitaxy (MBE), metal-organic chemical vapour deposition (MOCVD), and liquid-phase epitaxy (LPE). Each method produces the material with a specific defect structure, which may significantly affect the parameters of the final device. In this work, we report on the results of the comparative study of optical and structural properties of Hg$_{0.7}$Cd$_{0.3}$Te samples grown by various methods.

2. Experimental details

The core of the studied samples consisted of epitaxial films grown by MBE on (013)GaAs and (013)Si substrates with ZnTe and CdTe buffer layers at Rzhanov Institute of Semiconductor Physics (Russia) as described elsewhere [3]. LPE-grown films were fabricated with the use of closed-system epitaxy machines from Te-rich melts on (111)Cd(Zn)Te substrates according to the growth strategy presented in Ref. [4], and after the growth, these films were annealed in saturated Hg vapours at 230$^\circ$C for 48 hours. MOCVD–grown films were fabricated on Cd(Zn)Te–buffered semi-insulating 3$^\circ$-off (110)GaAs substrates at VIGO System S.A. (Poland) according to the interdiffused multi-layer
process described in Ref. [5]. The MOCVD process was completed with the deposition of a thin CdTe layer, which resulted in the formation of a ~0.5 μm–thick graded–gap surface layer during the cool–down step. No post–growth anneal was applied to these films. Bulk crystals were grown by the modified vertically directed crystallization (VDC) method with the replenishment from solid phase at Joint Stock Company ‘Pure Metals’ (Ukraine).

For optical studies, photoluminescence (PL) spectra were recorded in the $4.2 \rightarrow 300$ K temperature range with the use of an MDR-23 grating monochromator. The PL signal was excited by a semiconductor laser with 1.03 µm wavelength and registered with an InSb or HgCdTe photodetector. A DRON-8 X-ray diffractometer in a slit configuration with fine focus X-ray tube with a copper anode and a NaI(Tl) scintillation detector was used in the structural studies. Parameters of the studied samples are given in table 1. The chemical composition $x$ and the thickness of the MBE–grown films were assessed with the use of in situ ellipsometric [3] and ex situ optical transmission (OT) measurements, those of the LPE–and MOCVD–grown films, with OT and optical microscopy.

| Sample | Growth method | Substrate | $x$ | Film thickness, µm |
|--------|---------------|-----------|-----|--------------------|
| A      | MBE           | GaAs      | 0.32| 5.0                |
| B      | MBE           | GaAs      | 0.30| 8.2                |
| C      | MBE           | Si        | 0.32| 8.1                |
| D      | MBE           | Si        | 0.32| 8.1                |
| E      | MOCVD         | GaAs      | 0.32| 10.0               |
| F      | MOCVD         | GaAs      | 0.32| 9.2                |
| G      | LPE           | CdTe      | 0.32| 16                 |
| H      | LPE           | CdTe      | 0.29| 20                 |
| I      | VDC           | —         | 0.30| —                  |
| J      | VDC           | —         | 0.31| —                  |

3. Experimental Results and Discussion

OT spectra (not shown), which were recorded at 300 K with the use of an InfraLum-801 FTIR spectrometer, demonstrated high transmittance at the low-energy side and a relatively steep absorption feature when the photon energy became close to the $E_g$ for all the studied samples; these features were indicative of a good quality of the material. Figure 1 shows normalized PL spectra of samples B, C, D, E, H and J, recorded at 85 K. As can be seen, all the spectra with the exception of spectrum of sample E, represented single bands. The full-width at half-maximum (FWHM) of the spectra equalled 14.8 meV for sample A, 15.0 meV for samples B and C, 12.6 meV for sample D, 15.7 meV for samples I and J, and 19.4 meV for sample H. The FWHM of the high-energy (‘edge’) PL band of sample E equalled 23.9 meV; the low-energy band there could be related to optical transitions to acceptor levels induced by mercury vacancies.

At $T=4.2$ K, the FWHM of the spectra equalled 7.3 meV for sample C, 6.5 meV for sample D, 16.2 meV for sample E. For the films grown by MBE on Si substrates, in the low-temperature PL spectra we have not found any bands associated with energy states related to point defects. Such states were earlier believed to be typical of this material due to accumulation of point defects on extended defects that originated in substrate/film lattice mismatch [6], but they might as well be caused by non-optimal growth conditions [7].
Figure 1. Normalized photoluminescence spectra recorded at 85 K for samples B, C and D (a), and E, H and J (b) with thin lines showing fitting and decomposition of the spectrum E.

Figure 2 shows some examples of temperature dependences of the positions of the maxima of the ‘edge’ PL bands $E_{\text{PL}}(T)$ (symbols), which within the accuracy of $\sim$10 meV could be related to ‘optical’ bandgap $E_{\text{opt}}$ [8], and the $E_x(T)$ dependence calculated for MCT with $x$=0.32 in accordance with the most recent empirical $E_x(x,T)$ relation from Ref. [9]. As can be seen, the experimental dependences have similar slopes, but they differ from that of the calculated $E_x(T)$ relation. This trend was observed for all the samples and is due to the fact that optical transitions responsible for the ‘edge’ band were caused by recombination of excitons localized at compositional fluctuations; it is a typical feature of MCT that applies both to epitaxial films and bulk material [6,7,10,11]. The behaviour of $E_{\text{PL}}(T)$ for sample E may be related to the effect of the graded-gap surface layer and needs further investigation.

Of all the studied samples, only MBE-grown ones demonstrated PL signal at 300 K. This can be attributed to the presence of deep ‘technologically-induced’ fluctuations in addition to ‘stochastic’ ones, as these deep fluctuations facilitate stronger localization of excitons [6,7]. For LPE-grown samples, the PL signal disappeared at $T>150$ K.

Figure 2. Temperature dependences of the positions of the maxima of the ‘edge’ PL bands $E_{\text{PL}}(T)$ (symbols) for samples A, C and E, and $E_x(T)$ dependence calculated for $x$=0.32 according to reference [9] (line).

Figure 2(a) shows an XRD curve of sample I. It contained a single peak with $2\theta=23.79^\circ$ corresponding to (111) crystallographic HgCdTe plane. Its low intensity was indicative of relatively poor crystalline quality of the sample, which was confirmed by the absence of reflections from (222) and (444) planes. The XRD rocking curve (RC) of sample I (not shown) indicated the presence of multiple separate (111) blocks mis-oriented in relation to each other. The FWHM of this peak for sample B equalled 3236” (2$\theta$=97.81°), for sample C, 1038” (2$\theta$=97.76°).
The XRD curves of the LPE-grown films contained five peaks; Fig. 3(b) shows the curve for sample G. The first peak (peak I at 2θ≈21.52°) could be caused by oxidization of the surface of the sample or represent a by-product of the presence of the peak II at 2θ≈23.84° ((111)HgCdTe). The peak III at 2θ≈48.77° was caused by reflection from (222)HgCdTe plane, and peak V at 2θ≈111.25°, from (444)HgCdTe plane, with the intensity of the latter being higher than that of the former. The peak IV at 2θ≈76.51° corresponded to the reflection from (511)HgCdTe plane. Basically, both LPE-grown films showed a polycrystalline structure with (111)- and (511)-oriented blocks with single blocks showing high crystalline perfection, as the FWHMs of the peaks equaled 100-150''.

Thus, LPE-grown films showed higher crystalline quality than MBE-grown ones and even bulk crystals.

Figure 3. XRD curves of VDC-grown sample I and MBE-grown film C (inset) (a) and LPE-grown film G (b).

4. Conclusion
In conclusion, using optical and structural methods, we have studied properties of bulk crystals and epitaxial films of Hg$_{0.7}$Cd$_{0.3}$Te grown by various methods. The FWHMs of the ‘edge’ photoluminescence bands at 85 K were similar for all samples and varied from ~13 to ~20 meV. All the studied samples demonstrated $E_{PL}(T)$ slopes that differed from that of the calculated $E_g(T)$ relation. That, and the large gap between values of $E_{PL}$ and calculated $E_g$ at low temperatures clearly indicated the presence of alloy disorder. Most likely, it was this disorder that helped observing PL signal from MBE-grown samples at 300 K, and this makes MBE-grown material especially attractive for fabricating MWIR emitters, especially since despite the disorder this material did not show any excessive broadening of the spectra. The scale of the disorder seemed not to be directly related to the structural quality of the material as studied with XRD, so its nature and effect on the material properties other than optical (transport, etc.) require further investigations.

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