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Optical properties of indium-doped $Hg_{0.3}Cd_{0.7}Te$ epitaxial films

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The article presents the results of studying the optical properties of $Hg_{0.3}Cd_{0.7}Te$ films grown by molecular beam epitaxy and doped with indium. Optical reflectance and transmittance methods, as well as photoluminescence, are used for the study. According to the photoluminescence data, the introduction of indium lead to the formation of a donor level with an ionization energy of 10–12 meV. Films with an indium concentration $10^{16}-10^{17}\,cm^{-3}$ showed the stability of their optical properties during thermal annealing, including films in the $HgTe/Hg_{0.3}Cd_{0.7}Te$ heterocomposition. At indium concentrations $> 10^{18}\,cm^{-3}$, this stability is lost due to the interaction of the impurity with intrinsic defects.

Keywords: HgCdTe, doping, defects, photoluminescence.

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1. Introduction

Solid solutions of $Hg_{1-x}Cd_xTe$ (MCT) with a CdTe content (composition) $x \approx 0.7$ are in demand for the development of near-infrared photodetectors for astronomical observations [1,2] and in the creation of barrier layers of laser heterostructures [3,4], hybrid [5] and nBn photodetectors [6,7]. The material with the specified level of donor doping is necessary to manufacture both the photodetectors and the injection lasers. In MCT synthesis with the most in-demand method for today, molecular-beam epitaxy (MBE) method, implemented in the conditions of enrichment with tellurium, the films directly after growth (as-grown) usually already have the n-type of conductivity, provided by the presence of intrinsic defects and residual impurities. Concentration of electrons in such material, including that with $x \approx 0.7$, however, does not exceed $n \sim 10^{16}\,cm^{-3}$ [8]. To produce higher concentrations, intentional donor doping is required, and the most obvious (and traditional for MCT with $x < 0.5$) option here is introduction of indium [9–11]. The advantage of the doping with indium at low levels of doping, including doping in the MBE method, is high electrical activity and absence of electrical compensation causing stabilization and even decrease of n with increase of concentration of impurity C_{In} above certain limits. Both for MCT with $x \leq 0.4$ [9,10], and for CdTe [12,13] the level C_{In}, above which the compensation effect manifests, was determined as $\sim 10^{18}\,cm^{-3}$. However, data for doping of intermediate MCT compositions with indium is practically absent in the literature, and this is related to the studies of both electrical and optical properties of the material. In this paper we report the results of studies of the optical properties of the films grown by MBE method $Hg_{0.3}Cd_{0.7}Te$, doped with indium in the concentration range of $(0.02-4) \cdot 10^{18}\,cm^{-3}$.

2. Experimental procedure

Films with a thickness of $\sim 3\,\mu m$ were grown on (013) GaAs [14] substrates and had a constant composition (determined by *in situ* ellipsometry) across their thickness. Doping was carried out using indium flux from an additional source. Value C_{In} in the films was adjusted by the flux value specified by the change in the source temperature. Films were doped along the entire thickness, and the growth modes corresponded to the synthesis of undoped layers $Hg_{0.3}Cd_{0.7}Te$ in heterostructures HgTe/HgCdTe (they differ from the optimal ones due to substantial (by $\sim 100\,^{\circ}C$) difference of optimal MBE temperatures for HgTe and CdTe [15]). After growing the films had n-type conductivity; values n according to the Hall effect study data are given in the table; film A was undoped.

The film properties were studied by optical reflectance (OR), optical transmittance (OT) and photoluminescence (PL) methods. The OR and OT spectra were recorded at a temperature of $T = 293\,K$ using InfraLUM-801 Fourier spectrometer with a short-wave unit, or PerkinElmer Lambda 1050 grating spectrometer. PL spectra were recorded in temperature range $T = 4.2-293\,K$ using

Parameters of the studied samples

Sample No	Composition x	n, cm^{-3}
A	0.73	$\approx 1 \cdot 10^{14}$
B	0.71	$(1-2) \cdot 10^{16}$
C	0.71	$(4-5) \cdot 10^{17}$
D	0.72	$(2-4) \cdot 10^{18}$

MDR-23 monochromator with excitation by a semiconductor laser (wavelength $\lambda = 1.03\,\mu$m) and recording the signal with a germanium photodiode using lock-in detection. To determine stability of doped material properties in the course of the processes applied in manufacture of device structures, the film properties were also studied after two types of annealing. Annealing to generate mercury vacancies (used to obtain MCT of p-type conductivity) was carried out at temperature $T_{ann} = 410\,^{\circ}$C in helium atmosphere at lower pressure of mercury vapors for 7 min. Annealing to reduce the concentration of vacancy (used to obtain a material of n-type conductivity with minimum electrical compensation) was carried out for 24 h in inert atmosphere with saturated pressure of mercury vapors at $T_{ann} = 225\,^{\circ}$C. To imitate annealing of barrier layers from $Hg_{0.3}Cd_{0.7}Te$ in the composition of heterostructure HgTe/HgCdTe the layer of HgTe was applied on the surface of some specimens prior to annealing with thickness of 200 nm; the same layer is used to prepare Hall contacts.

3. Results and discussion

Figure 1 provides examples of film OR spectra A, B and D, recorded at $T = 293$ K after removal of HgTe layer. For comparison, OR spectra are also given for pure films CdTe, HgTe and $Hg_{1-x}Cd_xTe$ with $x = 0.75$, grown in the MBE conditions optimal for these materials. All spectra contain a specific doublet of peaks E_1 and $E_1 + \Delta$ (peaks are shown for some specimens), provided by optical transitions in points $\Lambda_{4,5} \rightarrow \Lambda_6$ and $\Lambda_6 \rightarrow \Lambda_6$ respectively [16,17]. Position of peaks E_1 and $E_1 + \Delta$ corresponded to the stated compositions of films (calculation of x according to OR data was made as per [18]). Low intensity of peaks E_1 and smearing of peaks in the spectra of the studied films $Hg_{0.3}Cd_{0.7}Te$ indicated disordering of the structure of their surface due to the specific nature of the growth conditions noted above. Increase in the level of doping did not manifest on the sharpness of peaks E_1, — spectra of all films, including an undoped film A, were similar.

Figure 2 provides the OT spectra of films recorded before and after annealing. The spectra are typical of structures based on MCT grown by the MBE [8,19] method; in the low-energy part, they are characterized by expressed interference fringes, indicating good planarity of the films. For film A without In after annealing a small high-energy shift of OT edge was observed, which is specific for the studied undoped material [8]. For films B and C, and also

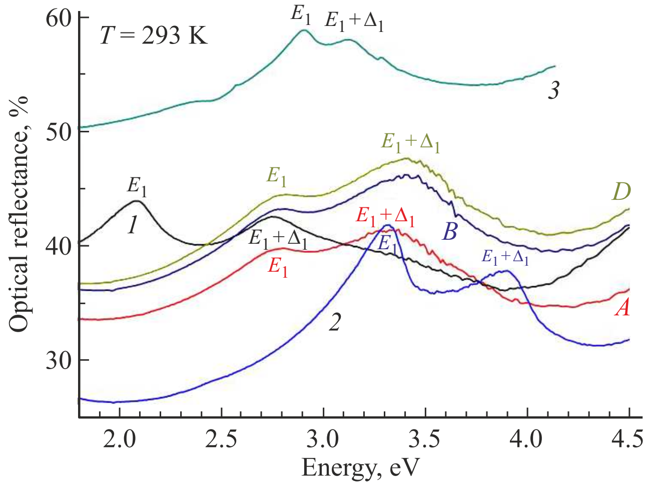

Figure 1. Spectra of optical reflectance of films A, B and D and reference specimens HgTe (spectrum *1*), CdTe (*2*) and $Hg_{1-x}Cd_xTe$ with $x = 0.75$ (*3*).

film D, annealed in the mode of vacancy filling after removal of HgTe layer, the position of OT edge after annealing did not change. Reduction in the transmittance value for film B after annealing was caused by deterioration of the surface quality. For film D, annealed in the mode of vacancy filling with the HgTe layer on the surface, a small shift of OT edge was observed towards lower energies.

Similar effects were observed for PL spectra of films recorded at $T = 103$ K; for example, Figure 3 shows spectra of films A and B. Here in Figure 3, a you can see that for the undoped film A after annealing to generate vacancies, a high-energy (by 19 meV) shift of PL spectrum maximum occurred; the half-width of the spectrum reduced from 32 to 20 meV. After annealing for filling vacancies the spectrum maximum shift (not shown) was slightly smaller, ~ 14 meV; such effect is typical of the studied material [20]. Figure 3, b, in its turn, shows that for film B lightly doped with indium as a result of annealing for filling vacancies after removal of HgTe layer the maximum of PL spectrum remained in place; its half-width reduced from 29 to 21 meV. After annealing with HgTe layer on the surface the PL spectrum either did not shift; its half-width reduced to 22 meV.

The PL spectrum recorded at $T = 103$ K for film C (not shown) also practically did not change its position after annealing; for film D, as in the case of OT edge, after annealing a low-energy (by ~ 30 meV) shift of PL peak was observed. It may be noted that for this film the PL spectrum recorded at 300 K (not shown), after annealings also slightly moved to the low-energy side. For films B and C the PL peak position at $T = 300$ K remained unchanged; in the combination with OT data (Figure 2) this meant invariability of their chemical composition after annealing. Changes in the PL spectra recorded at $T = 103$ K, mean the reduction in disordering (fluctuations of the composition) in the material not affecting the average value x. For the undoped film A PL signal at $T = 300$ K was not obtained; in the

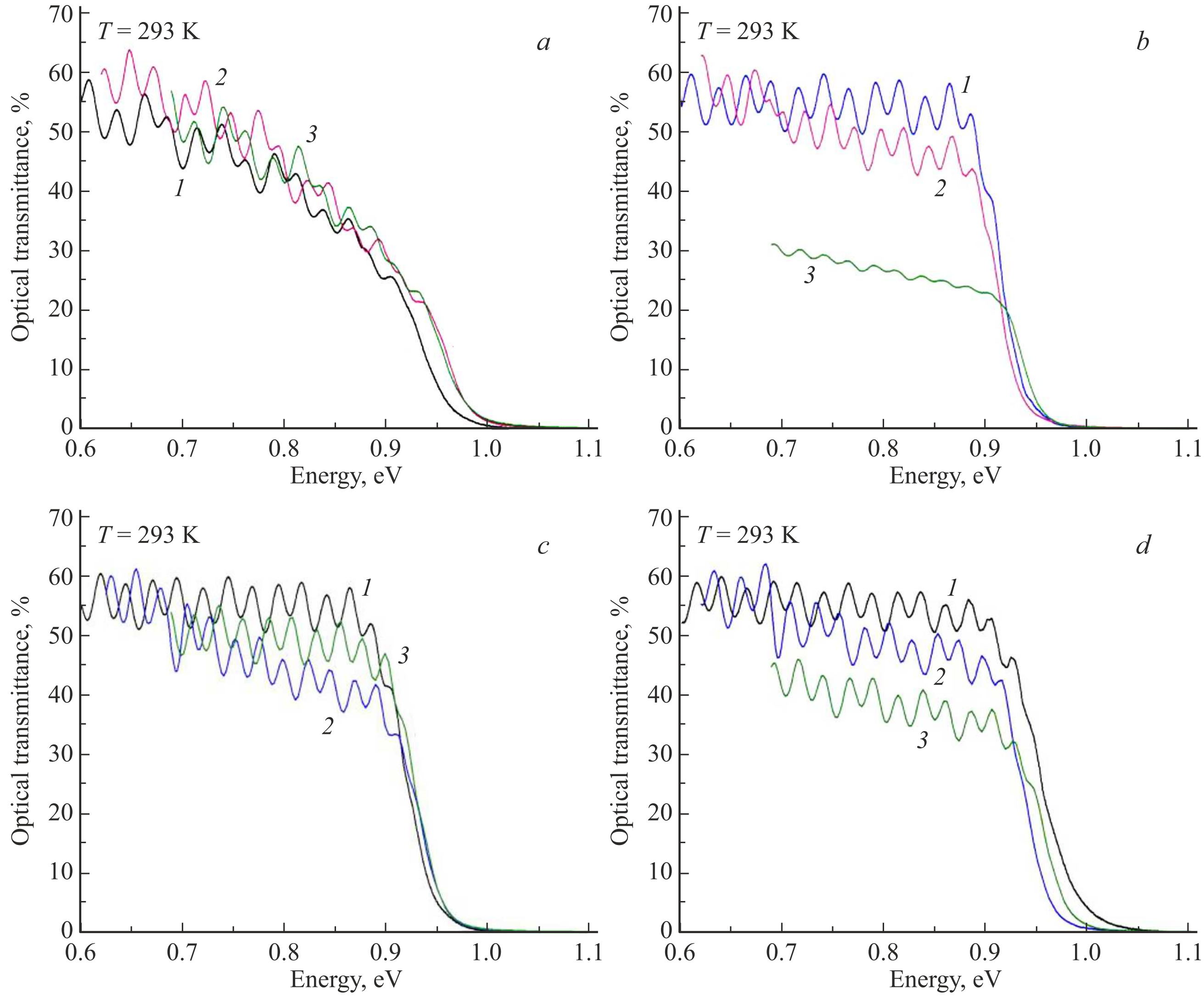

Figure 2. Spectra of optical transmittance before (*1*) and after annealing: *a* — film *A*: annealing for generation of (*2*) and filling (after removal of HgTe layer) of vacancies (*3*); *b, c* and *d* — films *B*, *C* and *D* respectively: annealing to fill vacancies with HgTe layer (*2*), and after removal of HgTe layer (*3*).

combination with somewhat smeared edge of OT for this film (Figure 2, *a*) this may mean a higher quality of the doped films.

Figure 4, *a* presents normalized PL spectra of the films recorded at $T = 4.2$ K. The initial spectra had various intensity; for convenience of perception the spectra were smoothened. For the undoped film *A* and lightly doped film *B* the spectra were well approximated by one band; its half-width was ~ 18 meV. Spectra of films *C* and *D* with high concentration of indium contained a marked low-energy feature, which could be related to impurity transitions provided for by the introduced indium. The precise analysis of the impurity line(s) position in the spectra was complicated due to intense effect of the water absorption bands in the atmosphere at their shape (so called „band φ“, $\lambda = 1.38\,\mu$m) and CO_2 ($\lambda = 1.40\,\mu$m). For the film *C* the distance of the impurity peak from „the edge one“ could be assessed as $\sim 10-12$ meV. Low-energy feature of the PL spectrum of film *D*, possibly, contained several lines, bound not only with the participation of the impurity level of indium, but with the levels of intrinsic defects and complexes formed due to high concentration of the impurity. Such pattern was observed many times for pure CdTe (see, for instance, [12,13,21]). Note that the assessment of the donor level position in CdTe in a simple hydrogen-like model provides the value 12 meV, the experiment — 14 meV [13,22]. For $Hg_{0.3}Cd_{0.7}Te$ the assessment provides the value ~ 7 meV. Acceptor states for these MCT compositions are substantially much deeper; their minimum energy of ionization may be assessed by extrapolating data [22,23] for $x \approx 0.7$, such as 55 meV for the intrinsic defects and 20 meV for the impurities.

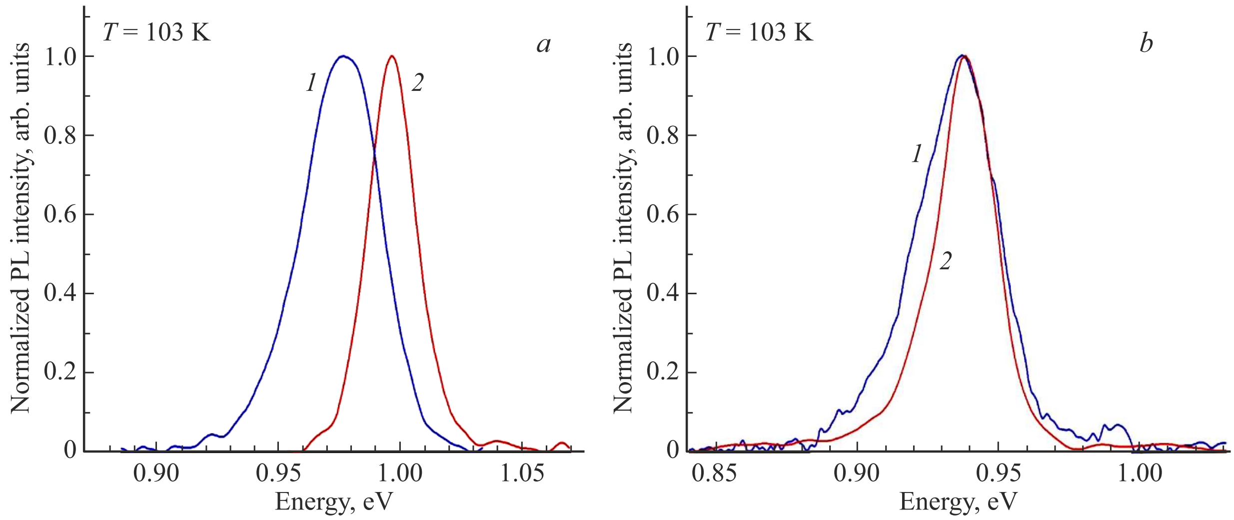

Figure 3. Normalized PL spectra ($T = 103$ K) of films A (a) and B (b before (1) and after (2) thermal annealing: for generation of vacancies with HgTe layer (film A) and for filling vacancies after removal of HgTe layer (film B).

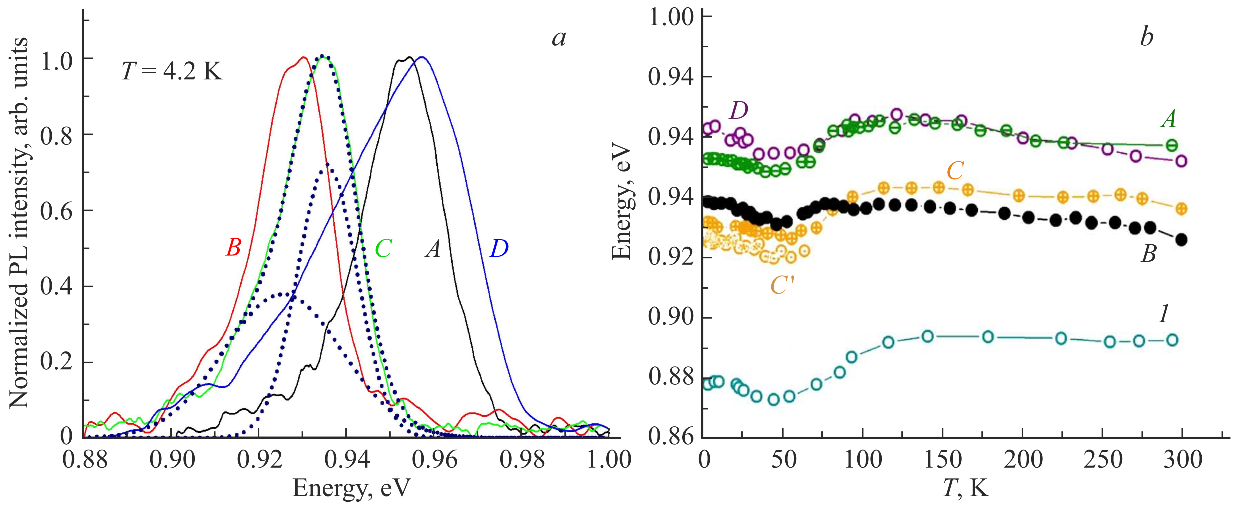

Figure 4. Photoluminescence spectra and temperature dependences of the peak position in „edge" PL of the studied films A, B, C (points show decomposition and adjustment of the spectrum) and D, and films with $x = 0.70$ from [24] (dependence 1) (b).

Figure 4, b shows the temperature dependences of the position of the „edge" PL peak in the studied films; for the film C the course of the similar dependence is also shown for the impurity peak (symbols C'). You can see that the dependences have a specific minimum at temperature 50−60 K, and after $T = 150$ K the peak energy with temperature increase starts gradually decreasing, as expected for MCT with $x > 0.5$. Such behavior is typical of the studied material [24,25]; for comparison, the figure contains the temperature dependence of the position of the „edge" PL peak of the film with $x = 0.70$ from [24] (dependence 1). Temperature trend of the impurity peak C' followed such of the „edge" peak.

Therefore, the results of the studies of the optical properties of the $Hg_{0.3}Cd_{0.7}Te$ films grown by the MBE method and doped with indium *in situ* showed that introduction of In results in formation of a donor level, the ionization energy of which may be assessed as 10−12 meV. In contrast to the undoped material, the films with $C_{In} = 10^{16}-10^{17}$ cm^{-3} demonstrate the resistance of the optical properties (position of the OT edge and PL spectra) to thermal annealing, including that in contact with the film of mercury telluride, imitating the quantum well from HgTe in the HgTe/HgCdTe heterostructure. This effect complies with the generally accepted ideas on the stabilized effect of presence of moderate ($10^{15}-10^{16}$ cm^{-3}) concentration of indium on electric properties of MCT [9] and photovoltaic properties of $p-n$-junctions on its basis [26]. At $C_{In} > 10^{18}$ cm^{-3} the resistance of the optical properties to the thermal annealing is lost, which is probably caused by interaction of the impurity with point defects and change in the nature of the diffusion processes under thermal treatment.

4. Conclusion

The methods of optical reflectance and transmittance and photoluminescence were used to investigate the optical properties of the $Hg_{0.3}Cd_{0.7}Te$ films grown by the method of molecular-beam epitaxy and doped with indium. According to the photoluminescence data, introduction of indium causes formation of a donor level in the films with ionization energy 10–12 meV. Films with indium concentration of $10^{16}-10^{17}\,cm^{-3}$ demonstrate the resistance of properties to the thermal annealing, including that within the heterocomposition HgTe/HgCdTe. At indium concentrations of $> 10^{18}\,cm^{-3}$ this resistance is lost due to the interaction of the impurity with the intrinsic defects. The produced results show the efficiency of the developed technology of HgCdTe donor doping of „large" ($x > 0.5$) compositions and serve as one more step towards creation of injection lasers and barrier photodetectors based on this material.

Conflict of interest

The authors declare that they have no conflict of interest.

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