

## Photoluminescence of arsenic doped epitaxial films of $\text{Cd}_{0.3}\text{Hg}_{0.7}\text{Te}$

© M.S. Ruzhevich<sup>1</sup>, D.D. Firsov<sup>2</sup>, O.S. Komkov<sup>2</sup>, K.D. Mynbaev<sup>1,3</sup>, V.S. Varavin<sup>4</sup>, M.V. Yakushev<sup>4</sup>

<sup>1</sup> ITMO University,

197101 St. Petersburg, Russia

<sup>2</sup> St. Petersburg State Electrotechnical University „LETI“,

197022 St. Petersburg, Russia

<sup>3</sup> Ioffe Institute,

194021 St. Petersburg, Russia

<sup>4</sup> Rzhanov Institute of Semiconductor Physics, Siberian Branch, Russian Academy of Sciences,

630090 Novosibirsk, Russia

E-mail: max.ruzhevich@niuitmo.ru

Received July 5, 2023

Revised September 5, 2023

Accepted September 7, 2023

The results of photoluminescence (PL) study of As-doped  $\text{Cd}_{0.3}\text{Hg}_{0.7}\text{Te}$  solid solutions films grown by molecular beam epitaxy on a Si substrate are presented. Analysis of the PL spectra obtained at different temperatures and excitation laser powers allows one to judge the nature of the observed peaks. The activation of arsenic in annealed samples was established, as a result of which shallow acceptor levels are formed. The effectiveness of arsenic as an acceptor impurity for cadmium-mercury tellurides has been confirmed.

**Keywords:** CdHgTe, doping, acceptor impurity, photoluminescence.

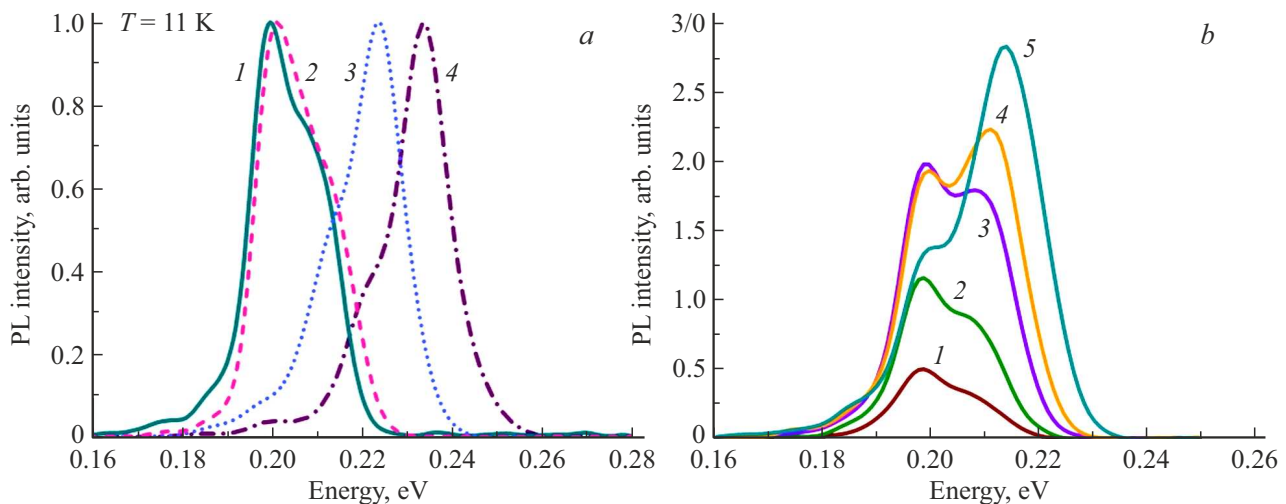
DOI: 10.61011/SC.2023.06.57170.5375

The formation of  $p-n$  junctions continues to be an urgent task for cadmium-mercury tellurides (CMT,  $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ ), one of the main materials of infrared photoelectronics, and, in particular, its medium-wavelength range (wavelengths  $\lambda = 3-5 \mu\text{m}$ ), where the material with  $x \approx 0.3$  [1] is used. Fabrication of the  $p-n$  structure implies the formation of regions with both electron and hole conductivity, but the problem of obtaining a CMT with  $p$ -type conductivity, especially using the method of molecular beam epitaxy (MBE), remains not completely solved. Currently, acceptor doping of MBE CMT with arsenic is generally accepted, however, immediately after growing  $\text{Cd}_x\text{Hg}_{1-x}\text{Te}:\text{As}$  films usually have an electronic conductivity [2]. It was believed that the reason for this is the amphoteric nature of arsenic, which can occupy both the lattice sites of the anion as an acceptor  $\text{As}_{\text{Te}}$  and the cation as a donor of  $\text{As}_{\text{Hg}}$  [3,4]. There is also an assumption about the existence of a chalcogenide glass type donor structure in MBE CMT  $\text{As}_2\text{Te}_3$  and an acceptor  $\text{AsHg}_8$  [5,6]. The mechanism of arsenic incorporation in MBE CMT remains a subject of discussion, but it is known that it is possible to obtain the  $p$ -type of conductivity by post-growth activation of the introduced impurity. It is performed by two-stage annealing, including the actual high-temperature ( $T \sim 350-400^\circ\text{C}$ ) activation and low-temperature ( $T \sim 200^\circ\text{C}$ ) annealing in saturated mercury vapors to reduce the concentration of mercury vacancies formed at high temperature.

Comparative analysis of photoluminescence (PL) of films  $\text{Cd}_x\text{Hg}_{1-x}\text{Te}:\text{As}$  before and after activation annealing was carried out repeatedly [7], but the data on the energy  $E_{\text{As}}$  of acceptor level formed during arsenic activation in

CMT with  $x \approx 0.3$  differ from 12.8 meV ( $\text{AsHg}$  complex,  $x = 0.30$  [8]) to 26.8 meV ( $\text{AsHg}_8$ ,  $x = 0.31$  [9]) and 11 meV for  $\text{As}_{\text{Te}}$  and 25 meV for the complex  $\text{As}_{\text{Hg}}-\text{V}_{\text{Hg}}$  ( $x = 0.30$  [10,11]). These data differ from the results of the Hall-effect measurements, according to which for CMT with  $x \approx 0.3$   $E_{\text{As}} \approx 6$  meV [12–14]. The results of the study of PL films  $\text{Cd}_{0.3}\text{Hg}_{0.7}\text{Te}:\text{As}$  grown by MBE on a Si substrate at the ISP SB RAS are reported in this paper. The composition ( $x \approx 0.29$ ) and thickness ( $d \approx 6 \mu\text{m}$ ) of the films were determined during growth using *in situ* ellipsometry [15]. The doping was carried out by a flux of arsenic from a Knudsen cell type source with a cracking zone installed on it. The doping level over the entire thickness of the films was set as  $2 \cdot 10^{16} \text{ cm}^{-3}$  for structure 1103 and  $5 \cdot 10^{16} \text{ cm}^{-3}$  for structure 1106. The growth regime of the structures remained the same as for undoped films of this composition [16]. The composition of the films and the absence of unintentionally introduced impurities were confirmed by examining the films *ex situ* on a TESCAN MIRA3 electron microscope with an UltiMAX energy dispersive X-ray detector.

Immediately after growing, the films had  $n$ -type of conductivity with electron concentration, according to the Hall-effect measurements at  $T = 77 \text{ K}$ ,  $(5-7) \cdot 10^{15} \text{ cm}^{-3}$  at mobility  $\sim 18000 \text{ cm}^2/(\text{V} \cdot \text{s})$ . Two-stage activation annealing carried out in saturated mercury vapor at  $T = 350^\circ\text{C}$  for 2 h and at  $T = 220^\circ\text{C}$  for 22 h, transferred the films to  $p$ -type with hole mobility  $\sim 190 \text{ cm}^2/(\text{V} \cdot \text{s})$  and their concentration  $9 \cdot 10^{15} \text{ cm}^{-3}$  for structure 1103 and  $5 \cdot 10^{16} \text{ cm}^{-3}$  for structure 1106. These data indicated good electrical activation of arsenic.



**Figure 1.** Normalized PL spectra at  $T = 11$  K films 1103 (1 and 4) and 1106 (2 and 3) before (1 and 2) and after (3 and 4) activation annealing (a), and the spectra of the unannealed film for 1103 at various values  $P_{ex}$ , mW: 1 – 7, 2 – 28, 3 – 72, 4 – 170, 5 – 400 (b).

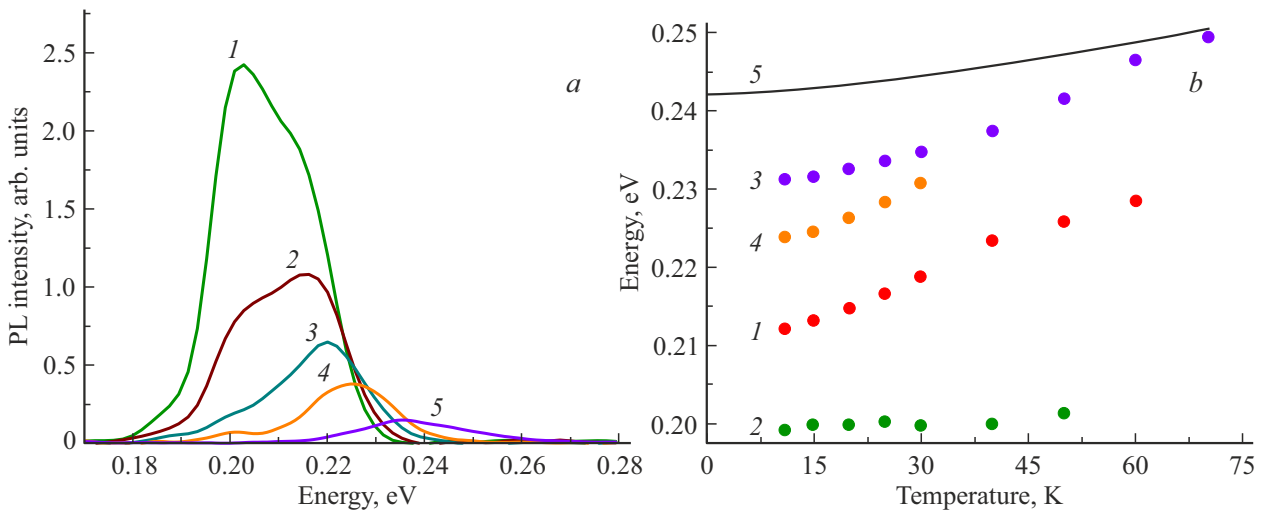
A facility based on the Vertex 80 Fourier spectrometer with step-by-step scanning, described in [17] was used to study the PL, in addition to the PL [18], this installation was also used for the studies of photoreflectance of graded-gap CMT-based structures. The excitation source was a diode laser with  $\lambda = 809$  nm. To exclude the impact of background thermal radiation, the PL spectra were recorded with lock-in amplification with mechanical modulation of laser radiation. The measurements were performed in the temperature range  $T = 11$ –294 K in a closed-cycle helium cryostat Janis CCS-150. The PL signal was recorded by a cooled photovoltaic detector based on CMT. To account for the effect of atmospheric absorption when processing the PL spectra, the latter were corrected using the glowbar spectrum recorded under the same conditions.

The optical transmission data (the spectra were recorded at  $T = 294$  K using the Fourier spectrometer InfraLUM-801) allowed us to clarify the composition of the films:  $x = 0.293$  for structure 1103 and  $x = 0.294$  for structure 1106; the uniformity of the composition over the area of the wafers was of  $\pm 0.003$ . Figure 1, a shows the PL spectra of films before and after annealing, recorded at  $T = 11$  K. The spectra contained two bands in all cases. The spectra 1 and 2 of films before annealing consisted of bands with a half-width of 10–12 meV with a peak distance of  $\sim 12$  meV. Figure 1, b shows a change in the shape of the PL spectrum of the film 1103 at different powers of the exciting laser  $P_{ex}$ . It can be seen that the spectral maximum shifted towards high energies with an increase of  $P_{ex}$ , the intensity of the high-energy (HE) band rapidly grew, and the intensity of the low-energy (LE) band was saturated. A slight shift of the PL bands occurred as a result of activation annealing (Figure 1, a), which is typical of the material under study [7]. The spectra 3 and 4 of annealed films were best described by two lines with a half-width of HE bands 8–9 meV and LE bands, 22–24 meV.

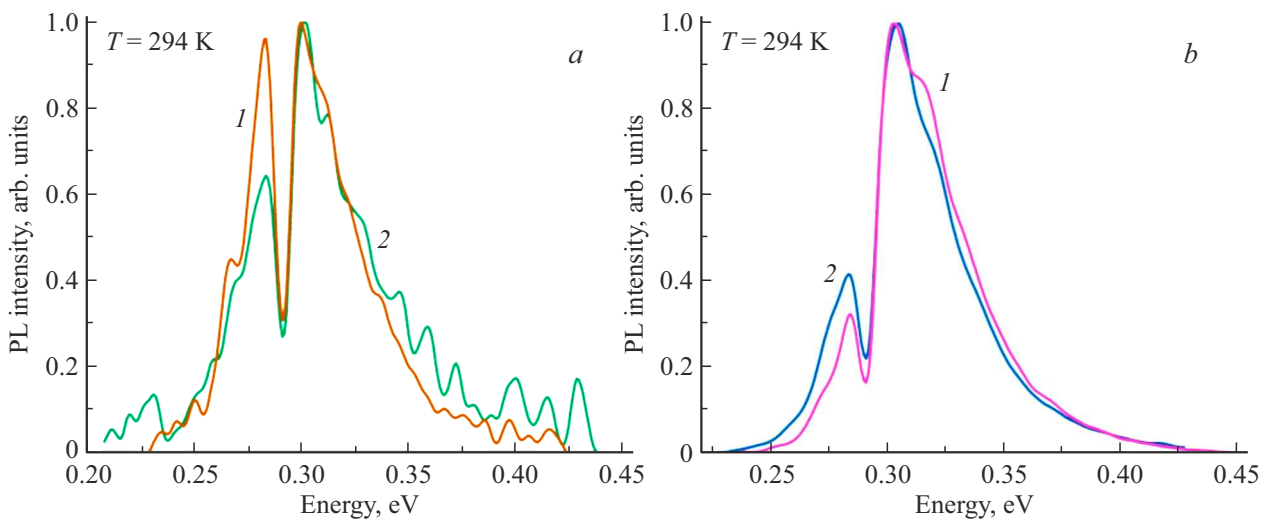
The distance between the HE and LE peaks at  $T = 11$  K was 7–8 meV. The intensities of the HE and LE peaks of annealed films with an increase of  $P_{ex}$  behaved like those of unannealed films.

The intensity of the PL LE bands of both films decreased significantly faster than the intensity of HE bands (Figure 2, a). LE bands were not registered at a temperature of  $> 50$  K. Figure 2, b shows the temperature dependences of the positions of the spectral maxima of the PL for structure 1103. The position of the HE peak of an unannealed film (see symbols 1) at low temperatures was significantly lower (by  $\sim 35$  meV at 11 K) than the values of the CMT band gap  $E_g$  with  $x = 0.293$ , calculated according to the data of [19] (curve 5). This energy difference (taking into account the increase  $x$ ) was smaller in an annealed film (symbols 3). The peak of the HE band began to approach the calculated values of  $E_g$  with an increase in temperature. The temperature dependence of the position of the LE peaks of the PL for the films was different: unannealed films (symbols 2) practically did not have such dependencies, while for the annealed films they were close to similar dependencies of the HE peaks.

Figure 3 shows the normalized PL spectra of the studied films at  $T = 294$  K. The PL intensity of annealed films was several orders of magnitude greater than that of unannealed films in absolute values. A dip in the spectra observed in the region  $\sim 0.29$  eV is associated with signal absorption by  $CO_2$  molecules in the atmosphere. It is possible to note the almost identical position of the PL bands for the two films, which confirms the similarity of their compositions, as well as a small HE shift of the PL peaks after activation annealing. The half-width of the PL bands before annealing was 54 and 60 meV, and it was 50 and 51 meV for films 1103 and 1106 after annealing, respectively.



**Figure 2.** *a* — PL spectra of the unannealed film 1106 at  $T, K$ : 1 — 11, 2 — 20, 3 — 30, 4 — 40, 5 — 80; *b* — temperature dependence of PL peak positions for 1103 film at low temperatures: before (1 and 2) and after (3 and 4) annealing, 5 — calculated dependence  $E_g(T)$ .



**Figure 3.** Normalized PL spectra at  $T = 294 K$  of unannealed (*a*) and annealed (*b*) films 1103 (1) and 1106 (2).

The data obtained suggest that both before and after the annealing of the films the HE bands of both films corresponded to interband optical transitions, while the LE bands in the films before and after annealing had a different nature. The LE bands in films before the annealing were most likely attributable to donor-acceptor recombination (DAR). Their position relative to the HE bands, half-width, and behavior with changes in external conditions were similar to those observed earlier for DAR in undoped CMT [20] films with  $x = 0.32$ , also grown on Si substrates. This circumstance does not allow unambiguously linking the manifestation of the donor level with the doping of the studied films with arsenic, although such an interpretation is possible. The energy values of a similar level of 15.2 meV for  $As_2Te_3$  and 11.8 meV for  $As_{Hg}$  ( $x = 0.31$ ) [9], 8.5 meV [10] and 17 meV [11]

for  $As_{Hg}$  ( $x = 0.30$ ) obtained on the basis of the PL data are provided in the literature. However, classical representations of the donor in the CMT with  $x = 0.30$  in the framework of the hydrogen-like model give energy  $\sim 0.85 meV$  [21]; such a level could participate in the observed DAR. As for the LE bands in the spectra of annealed films, their nature is different from DAR and corresponds to the behavior of a typical acceptor, noting the fact that acceptor states with similar energies in undoped samples grown using this technology have not been previously observed [7]. The occurrence of these bands can be attributed to energy levels formed as a result of arsenic activation. The obtained energy values ( $\sim 7-8 meV$ ) are consistent with the above-mentioned data from studies of both PL [9,11] and the Hall effect [12-14] in  $Cd_{0.3}Hg_{0.7}Te:As$ .

Thus, we conducted a study of the photoluminescence of arsenic-doped CMT films grown by MBE on a Si substrate. It was established that shallow acceptor states with activation energies of 7–8 meV are formed as a result of arsenic activation. The achievement of a high degree of electrical activation of arsenic in combination with the shallow depth of the energy level confirms its effectiveness as an acceptor dopant in the CMT.

### Conflict of interest

The authors declare that they have no conflict of interest.

### References

- [1] M. Kopytko, A. Rogalski. *Sensors Actuators: A. Phys.*, **339**, 113511 (2022).
- [2] J.W. Garland, C. Grein, S. Sivananthan. *J. Electron. Mater.*, **42**, 3331 (2013).
- [3] M.A. Berding, A. Sher. *Appl. Phys. Lett.*, **74**, 685 (1999).
- [4] H.R. Vydyanath. *Semicond. Sci. Technol.*, **5**, S213 (1990).
- [5] X. Biquard, I. Alliot, P. Ballet. *J. Appl. Phys.*, **106**, 103501 (2009).
- [6] P. Ballet, B. Polge, X. Biquard, I. Alliot. *J. Electron. Mater.*, **38**, 1726 (2009).
- [7] M.S. Ruzhevich, K.D. Mynbaev. *Rev. Adv. Mater. Sci. Technol.*, **4** (4), 17 (2022).
- [8] I.C. Robin, M. Taupin, R. Derone, A. Solignac, P. Ballet, A. Lussion. *Appl. Phys. Lett.*, **95**, 202104 (2009).
- [9] F. Gemain, I.C. Robin, S. Brochen, P. Ballet, O. Gravrand, G. Feuillet. *Appl. Phys. Lett.*, **102**, 124104 (2013).
- [10] F. Yue, J. Chu, J. Wu, Z. Hu, Y. Li, P. Yang. *Appl. Phys. Lett.*, **92**, 121916 (2008).
- [11] F.-Y. Yue, L. Chen, Y.-W. Li, Z.-G. Hu, L. Sun, P.-X. Yang, J.-H. Chu. *Chin. Phys. B*, **19**, 117106 (2010).
- [12] G.K.O. Tsen, R.H. Sewell, A.J. Atanacio, K.E. Prince, C.A. Musca, J.M. Dell, L. Faraone. *Semicond. Sci. Technol.*, **23**, 015014 (2008).
- [13] M. Zandian, A.C. Chen, D.D. Edwall, J.G. Pasko, J.M. Arias. *Appl. Phys. Lett.*, **71**, 2815 (1997).
- [14] Y. Selamet, C.H. Grein, T.S. Lee, S. Sivananthan. *J. Vac. Sci. Technol. B*, **19**, 1488 (2001).
- [15] M.V. Yakushev, V.S. Varavin, V.G. Remesnik, D.V. Marin. *Semiconductors*, **48**, 767 (2014).
- [16] G.Yu. Sidorov, N.N. Mikhailov, V.S. Varavin, D.G. Ikusov, Yu.G. Sidorov, S.A. Dvoretiskii. *Semiconductors*, **42**, 651 (2008).
- [17] D.D. Firsov, O.S. Komkov, V.A. Solov'ev, P.S. Kop'ev, S.V. Ivanov. *J. Phys. D: Appl. Phys.*, **49**, 285108 (2016).
- [18] O.S. Komkov, M.V. Yakushev. *Semiconductors*, **57** (6), 425 (2023).
- [19] C.R. Becker, V. Latussek, A. Pfeuffer-Jeschke, G. Landwehr, L.W. Molenkamp. *Phys. Rev. B*, **62**, 10353 (2000).
- [20] K.D. Mynbayev, N.L. Bazhenov, V.I. Ivanov-Omsky, V.A. Smirnov, M.V. Yakushev, A.V. Sorochkin, V.S. Varavin, N.N. Mikhailov, G.Yu. Sidorov, S.A. Dvoretzky, Yu.G. Sidorov. *Tech. Phys. Lett.*, **36**, 1085 (2010).
- [21] D. Shaw, P. Capper. *Extrinsic Doping*, Chap. 14 in: *Mercury cadmium telluride: growth, properties, and applications*, ed. by P. Capper, J. Garland (John Wiley & Sons Ltd., Chichester, 2017) p. 323. <https://doi.org/10.1002/9780470669464>

*Translated by A.Akhtyamov*