

PHOTOLUMINESCENCE OF $\text{Hg}_{0.5}\text{Cd}_{0.5}\text{Te}$ STRUCTURES GROWN WITH MOLECULAR-BEAM EPITAXY

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Abstract. Photoluminescence (PL) of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ -based ($x \sim 0.5$) structures grown with molecular-beam epitaxy on GaAs and Si substrates was studied. The studied structures appeared to have substantial compositional fluctuations, which at low temperatures ($T < 200$ K) strongly affected the value of “optical” bandgap obtained in the experiment. Comparison of the experimental results with the data available in the literature showed that such fluctuations were in general typical of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ with $x \sim 0.5$ fabricated with various technologies. At $T > 200$ K the effect of the fluctuations on the optical properties of the studied material became negligible, which confirmed that the structures were suitable for fabrication of photo-electronic devices operating in the extended short-wave infrared range.

1. Introduction

For the last 50 years, $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ (MCT) solid solutions have remained one of the basic materials for fabricating infrared (IR) photodetectors. So far, the most widely studied was narrow-gap $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ with chemical composition (CdTe molar fraction) $x \approx 0.2$ or $x \sim 0.3$ – 0.4 , as the energy bandgap E_g of such material corresponds to the energy of photons in long-wavelength (8–14 μm) and middle-wavelength (3–5 μm) IR ranges, respectively [1–3]. MCT with $x \geq 0.5$ (wavelengths < 2 μm) up to now has not been studied in so much detail. Recently, however, there has been some interest in wide-bandgap MCT due to the development of photodetectors for so-called ‘extended Short-Wave IR’, eSWIR range (wavelengths 1.7–3.0 μm) [4–8]. Employing commonly used SWIR materials (such as InGaAs grown on InP substrate) when moving towards longer wavelengths faces substantial reduction in quantum efficiency of hetero-junction devices, which is caused by a very large band offset at the hetero-interfaces and increase in defect density due to enlarged lattice mismatch [9,10].

One of the most informative methods of the characterization of semiconductor materials is photoluminescence (PL). In regards to MCT, up to now PL has been mostly used for studying the properties of material with $x \sim 0.3$ – 0.4 . This is due to the fact that MCT with smaller x suffers from a strong influence of non-radiative recombination, while the material with $x > 0.5$, as already mentioned, so far has not been of much practical interest. The data on PL in MCT

with $x \sim 0.5$ available in the literature [11–17] were obtained (with the exception of Ref. [17]) on the samples, which were fabricated at the early stages of MCT technology (1980–1990) with methods of bulk crystal growth (solid–state re–crystallization, traveling heater method, etc.) and liquid–phase epitaxy. Currently, the most popular method of the synthesis of MCT is molecular–beam epitaxy (MBE), which allows for fabricating both homo– and hetero–epitaxial structures (HES) with precise control over the thickness of the layers and the level of doping [18, 19]. MCT grown with MBE has been shown to exhibit substantial compositional fluctuations, which strongly affected the optical properties of the material [20–22]. The effect of the fluctuations has been studied in detail for MCT with $x \sim 0.3$ – 0.4 , while for the material with $x \sim 0.5$ there is still not much data available. In this paper, we report on the studies of PL of MBE–grown Hg_{1-x}Cd_xTe with the chemical composition of the ‘absorber’ layer of the HES x_a ranging from 0.47 up to 0.58 (E_g of such material corresponds to the energy of photons relating to the wavelength range 1.6–2.2 μm at the temperature $T = 300$ K).

2. Experimental technique

The HES were grown on (013)Si or (013)GaAs substrates at the Rzhanov Institute of Semiconductor Physics with the use of the method described elsewhere [19]. ZnTe and CdTe buffer layers were used. The structures had ‘absorber’ layers with uniform composition with thickness d ranging from 1 up to 8 μm . The values of x_a in this layer as defined with ellipsometry measurements performed *in situ* are shown in Table 1. On top of the ‘absorber’ layer, a graded–gap protective layer was grown with the thickness ~ 1.0 μm and chemical composition increasing towards the surface up to $x \sim 0.7$ – 0.8 . After the growth, the samples were of *n*–type conductivity with typical electron concentration as measured with the use of the Hall effect at $T = 77$ K, $(5\text{--}10) \times 10^{14}$ cm^{-3} . For PL studies, samples with ~ 0.3 cm^2 area were cut out from the HES. PL signal was excited by a semiconductor laser with the wavelength 1.03 μm and was registered with a Ge photodetector with the use of a lock–in amplifier.

Table 1. Parameters of the studied HES.

HES No.	Substrate	x_a
0814	Si	0.47
0318		0.58
0829	GaAs	0.49
0903		0.54
1215		0.57

3. Results and discussion

Some examples of PL spectra of HES which were grown on GaAs and Si substrates are presented in Fig. 1. The spectra were recorded at $T = 77$ K. It is of common belief that in low–temperature PL spectra of MCT the dominating band is that of recombination of exciton localized at compositional fluctuations [13, 15, 16, 20–22]. The energy states due to fluctuations define the position of the luminescence peak, so its shift relative to the calculated value of energy bandgap E_{gcal} is a sort of measure of the scale of the fluctuations. At the same time, when dealing with narrow–bandgap semiconductors under strong excitation, strictly speaking one cannot relate the energy of luminescence peak E_{PL} directly to the energy band of the semiconductor. The actual peak is shifted towards higher energies, and the larger is concentration of equilibrium and non–equilibrium charge carriers, the larger is the shift. So, to accurately determine the value of ‘optical’ bandgap E_{gopt} one should calculate the luminescence spectrum and fit its high–energy part to that of the experimental one with carrier concentration

being a fitting parameter. The point where the low-energy part of the calculated spectrum crosses the energy axis will correspond to E_{gopt} .

The correct description of optical transitions in MCT requires consideration of transitions of electrons to the bands of both heavy and light holes; also, non-parabolic dependence of energy on the wave vector should be considered for electrons and light holes. The transition matrix element for such a case was calculated in Ref. [23]. So, for luminescence intensity I we have:

$$I(\hbar\omega) \propto \omega^2 (\alpha_{hh}^0 f_n^h f_p^h + \alpha_{lh}^0 f_n^l f_p^l), \quad (1)$$

where

$$\alpha_{hh}^0 = \frac{\sqrt{2}e^2}{\hbar^2 c \sqrt{\varepsilon}} \sqrt{\frac{m_e}{E_g}} \sqrt{(\hbar\omega - E_g)\hbar\omega}, \quad f_n^h = \left\{ 1 + \exp \left[\frac{\hbar\omega - E_g}{kT} \left(1 - \frac{m_e \hbar\omega}{m_h E_g} \right) - \frac{\xi_e}{kT} \right] \right\}^{-1},$$

$$f_p^h = \left\{ 1 + \exp \left[\frac{\hbar\omega}{kT} \frac{m_e}{m_h} \left(\frac{\hbar\omega - E_g}{E_g} \right) - \frac{\xi_h}{kT} \right] \right\}^{-1}, \quad \alpha_{lh}^0 = \frac{e^2}{6\sqrt{2}\hbar^2 c \sqrt{\varepsilon}} \sqrt{\frac{m_e}{E_g}} \sqrt{(\hbar\omega^2 - E_g^2)},$$

$$f_n^l = \left\{ 1 + \exp \left[\left(\frac{\hbar\omega - E_g}{2kT} \right) - \frac{\xi_e}{kT} \right] \right\}^{-1}, \quad f_p^l = \left\{ 1 + \exp \left[\left(\frac{\hbar\omega - E_g}{2kT} \right) - \frac{\xi_h}{kT} \right] \right\}^{-1}.$$

Here, e is the electron charge; ε is the permittivity; m_h is the effective mass of a heavy hole; m_e is the effective mass of an electron and (according to the Kane model) the mass of a light hole; ξ_e and ξ_h are the quasi-Fermi levels of electrons and holes measured from the edges of the relevant bands. Expressions (1) hold true for an arbitrary degeneracy factor for both electrons and holes.

Under assumption that we have high level of excitation in our experiment, concentrations of non-equilibrium electrons and holes are almost the same: $\Delta n \approx \Delta p \gg n_0, p_0$ (n_0 and p_0 represent carrier concentration under equilibrium, while Δn and Δp designate the excessive carrier concentration under the injection). This allows for estimating ξ_e and ξ_h and for calculating the spectrum. Figure 1 shows calculated luminescence spectra along with the experimental ones. The value of the carrier concentration used for fitting the spectra at $T = 77$ K varied in the range $(6-12) \times 10^{16} \text{ cm}^{-3}$ for various samples. This meant that the condition $\Delta n, \Delta p \gg n_0, p_0$ certainly held true. Note, however, that the best fit also required some corrections in the chemical composition of the samples. For example, instead of nominal values (those obtained with ellipsometric measurements *in situ*) of 0.49 and 0.58 for samples 0829 and 0318 we had to use values of 0.47 and 0.57, respectively.

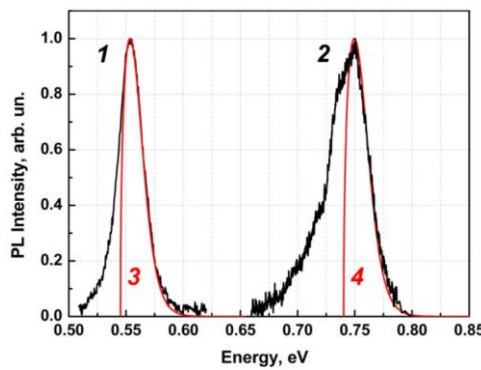


Fig. 1. Experimental (curves 1 and 2) and calculated (3 and 4) normalized PL spectra of samples 0829 (GaAs substrate, curves 1 and 3) and 0318 (Si substrate, curves 2 and 4) at $T = 77$ K.

As follows from Fig. 1, the difference between E_{PL} and E_{gopt} of the ‘absorber’ layer of HES, as determined with the method described above, did not exceed 10 meV, and therefore, considering the nominal value of E_g of the studied samples of 500–800 meV, the values of E_{PL} gave satisfactory approximation to E_{gopt} . Figure 2 shows temperature dependencies of E_{gopt} , which were derived from the experimental PL data, and calculated dependencies $E_{gcal}(T)$ for

the samples with a given x_a (E_{gcal} was calculated according to empirical $E_g(x,T)$ dependence from Ref. [24]). As can be seen in Fig. 2, for the studied HES at $T < 100$ K there was a considerable difference between the slope of the temperature dependence of E_{PL} and that of $E_{gcal}(T)$. Again, this is commonly explained by the fact that at low temperatures PL spectra of MCT are dominated by the band due to radiative recombination of exciton localized at compositional fluctuations [13, 15, 16, 20–22]. It is also believed that at temperatures approaching 300 K, inter-band transitions involving free carriers dominate in MCT [15]. If we assume that at these temperatures the values of E_{PL} actually correspond to E_g [20, 25], then the x_a values for samples 0829 and 0814 can be determined from PL spectra at $200 < T < 300$ K as 0.46 and 0.48, respectively, and are in a good agreement with nominal x values. At the same time, at the temperatures close to that of liquid helium, the difference $E_{gcal} - E_{PL}$, for example, for samples 0829 and 0814, equals 68 and 70 meV, respectively. Figure 2 also shows experimental data from Refs. [11], [14] and [15] that were obtained on *as-grown* MCT samples with similar chemical composition, which were grown with solid-state re-crystallization ($x = 0.48$) [11] and liquid-phase epitaxy ($x = 0.50$) [14]. As can be seen, experimental E_{PL} values obtained on the samples grown with the latter methods at low temperatures are closer to calculated E_g values than those of E_{PL} obtained on the samples grown with MBE, yet the difference $E_{gcal} - E_{PL}$ is still considerable: for the sample with nominal composition 0.48 [11] it equals 35 meV, while for the sample with $x = 0.50$ [14], 40 meV. This difference is small (~ 14 meV) only for the sample with $x = 0.50$, which was studied in Ref. [15], yet the fact that the energy of PL peaks for this sample at $T = 100$ K and higher temperatures exceeds E_{gcal} is indicative of the problems with correct determination of the chemical composition.

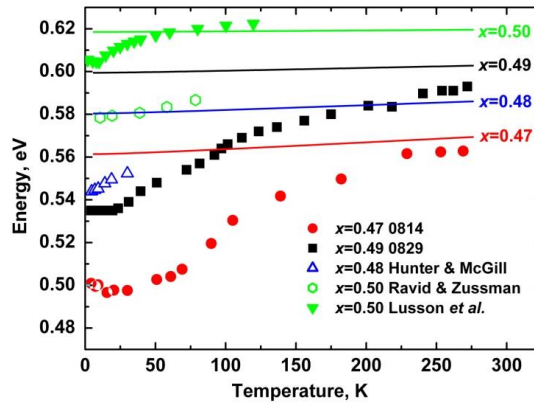


Fig. 2. Calculated dependencies $E_{gcal}(T)$ for MCT with various compositions (straight lines) and experimental dependencies $E_{PL}(T)$ for the samples 0814 (Si substrate) and 0829 (GaAs substrate) and according to the data from Refs. [11,14, 15] (symbols).

In Refs. [22, 26], a modeling of compositional fluctuations in MCT was performed and the obtained data were related to experimental values of $E_{gcalc} - E_{PL}$ that were acquired in PL studies of MCT at low temperatures. In particular, it was shown in Ref. [22] that samples grown with the methods employed for the synthesis of bulk crystals and with liquid-phase epitaxy, as a rule, have smaller scale of compositional fluctuations than those grown with MBE. In general, this conclusion holds true for the samples studied in this work as well. Figure 3 shows values of $E_{gcalc} - E_{PL}$ at $T=4.2$ K, which were obtained for the samples studied in this work, for MBE-grown samples from Ref. [22], and for MCT bulk crystals and layers grown with liquid-phase epitaxy and studied in Refs. [11, 14, 15]. (In contrast to approach used in Ref. [22], in this figure only values of $E_{gcalc} - E_{PL}$ are plotted rather than “exciton binding energy”, which was defined by various authors with the use of different methods.)

It is obvious in Fig. 3 that for chemical composition range considered in this work, samples grown with MBE typically have greater fluctuation scale than bulk crystals or layers

grown with liquid–phase epitaxy. At the same time, the difference in $E_{gcalc}-E_{PL}$ values for the two groups of samples is not that large: for MBE–grown samples in general it equals ~ 60 meV, while for bulk crystals and layers grown with liquid–phase epitaxy, ~ 45 meV. For samples with $x < 0.4$ this difference was much larger, the corresponding values were 35 meV and 10 meV, respectively [22]. Therefore, compositional fluctuations, which we observed for MCT samples studied in this work, appear to be typical of $Hg_{1-x}Cd_xTe$ with $x \sim 0.5$, and are not related to the specifics of MBE technology to such an extent as it was the case for the material with low x values.

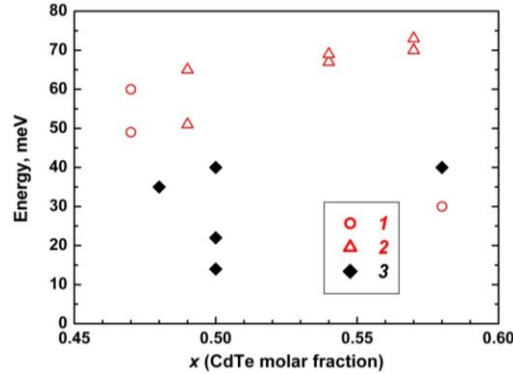


Fig. 3. Experimental values of $E_{gcalc}-E_{PL}$ at $T=4.2$ K for the samples studied in this work and in Ref. [22] (1, HES grown on Si substrate, 2, HES grown on GaAs substrate) and similar values for non-MBE-grown MCT extracted from the literature (3).

One of the reasons for this may be the fact that purely stochastic distribution of atoms between the different lattice sites gives the maximum fluctuation scale for solid solutions where substitution of cation sublattice sites with metals (Cd and Hg in MCT) is of equal probability, *i.e.*, for samples with $x=0.50$. For more detailed analysis of this problem it would be desirable to perform a similar study on the samples with $x > 0.6$, where the scale of purely stochastic fluctuations should begin to decline; for such samples grown with MBE the available data on $E_{gcalc}-E_{PL}$ are not yet sufficient. It is important, however, that according to the data presented in Fig. 2, at $T > 200$ K the effect of the fluctuations on the optical properties of the studied material becomes insignificant, as the energy bandgap (and the corresponding value of chemical composition of the solid solution) derived from the PL data approaches its nominal value that was set during the growth and controlled with ellipsometric measurements. This confirms the possibility of the use of MBE–grown $Hg_{1-x}Cd_xTe$ with $x \sim 0.5$ in photo–electronic devices of eSWIR range, as the working temperature of such devices typically exceeds 200 K [4–8].

4. Conclusion

In this work, the results of the studies of photoluminescence (PL) of the $Hg_{0.5}Cd_{0.5}Te$ structures grown with molecular-beam epitaxy on GaAs and Si substrates were presented. By relating the experimental PL spectra to those obtained with calculations it was shown that the structures possessed substantial fluctuations of chemical composition, which at low temperatures ($T < 200$ K) significantly affected the ‘optical’ bandgap registered with PL measurements. However, comparison of the data obtained with PL data taken from the literature has shown that the observed effect is typical of $Hg_{1-x}Cd_xTe$ with $x \sim 0.5$ in general, and is not specific for a growth technology. At $T > 200$ K the effect of fluctuations on the optical properties of the studied material became insignificant, which confirmed the possibility of using molecular–beam epitaxy–grown MCT in photo–electronic devices operating in the extended short–wave infrared range.

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