
Proc. XXXVII International School of Semiconducting Compounds, Jaszowiec 2008

Epitaxial Growth and Optical Properties of PbTe/CdTe Semiconductor Heterostructures

M. SZOT, L. KOWALCZYK, E. SMAJEK, V. DOMUKHOVSKI,
J. DOMAGAŁA, E. ŁUSAKOWSKA, B. TALIASHVILI, P. DZIAWA,
W. KNOFF, M. WIATER, T. WOJTOWICZ AND T. STORY

Institute of Physics, Polish Academy of Sciences
al. Lotników 32/46, 02-668 Warsaw, Poland

Growth optimization, optical and structural properties of PbTe/CdTe multilayers grown by molecular beam epitaxy on GaAs (001) as well as on BaF₂ (111) substrates is reported. An intense photoluminescence in the mid-infrared region is observed from PbTe quantum wells excited with 1.17 eV pulsed YAG:Nd laser. The energy of the emission peak shows blue shift with decreasing PbTe well width and has a positive temperature coefficient. The influence of thermal annealing on photoluminescence spectra of PbTe/CdTe multilayers grown on BaF₂ substrate is discussed.

PACS numbers: 78.55.Hx, 78.67.De, 78.67.Hc, 78.67.Pt

1. Introduction

The availability of very efficient optoelectronic devices active in the mid-infrared region is crucial for many applications in medicine, environmental protection or molecular spectroscopy. In this spectral region low-dimensional structures based on IV–VI semiconductors like PbTe, are attractive candidates for room temperature operating detectors and light sources. In the last few years, high crystal and optical quality PbTe/CdTe structures containing single PbTe quantum well [1, 2] or single layer of isotropic PbTe quantum dots [3, 4] were successfully grown by molecular beam epitaxy (MBE) on GaAs substrates. Because of large difference between GaAs and PbTe lattice parameters ($\approx 13\%$), complicated buffer layer (CdTe/MnTe strained-layer superlattice) was implemented in these structures. On the other hand, PbTe and CdTe semiconductor materials exhibit excellent matching of their lattice parameters but crystallize in different cubic lattices: zinc blende ($a_0 = 6.48 \text{ \AA}$) for CdTe and rock salt ($a_0 = 6.46 \text{ \AA}$)

for PbTe. This difference in lattice structure results in a large miscibility gap in the case of CdTe and PbTe materials. Simultaneously, properties of PbTe/CdTe interfaces were studied theoretically [5] and experimentally using high-resolution transmission electron microscopy (HRTEM) [3, 6].

In PbTe/CdTe heterostructures, narrow gap PbTe ($E_{g,300\text{K}} = 0.3$ eV at L point of the Brillouin zone) constitutes quantum well or quantum dot material with wide gap CdTe ($E_{g,300\text{K}} = 1.5$ eV at Γ point of the Brillouin zone) electronic barriers. The large discrepancy in band gap energies of CdTe and PbTe semiconductors leads to a very efficient carrier confinement, making structures with PbTe quantum dots highly luminescent at room temperature [3].

Recently, GaAs substrate with thick, monocrystalline CdTe buffer layer was used for fabrication of PbTe quantum dots with controlled spatial sizes [7]. In this paper we describe growth of PbTe/CdTe multilayers on GaAs (001) and BaF₂ (111) substrates using CdTe as buffer layer in both cases of structures. The study of basic optical properties of obtained PbTe/CdTe structures in the mid infrared region and influence of annealing on luminescence are also presented.

2. Experimental

Various PbTe/CdTe multilayers were grown by molecular beam epitaxy using compound PbTe and CdTe sources. Two kind of substrates, i.e. semi-insulating (100) oriented GaAs with high quality monocrystalline CdTe buffer layer and (111) oriented BaF₂ with PbTe or CdTe buffer were used. In the case of GaAs-deposited structures 4 μm thick buffer was used because of large GaAs and CdTe lattice parameters and thermal expansion coefficients misfit. Since for BaF₂ and CdTe the lattice constants difference is smaller, 1 μm thick buffer layer was used in the case of structures deposited on BaF₂.

The PbTe/CdTe heterostructures were grown at substrate temperature varying in the range 200–340°C. At first, the samples with single PbTe or CdTe layers with thicknesses up to 1 μm were grown for the optimization of the growth process. Thereafter, the multi-quantum well (MQW) structures with layer thickness covered the range $t = 6$ –20 nm for PbTe layers and $d = 7$ –50 nm for CdTe barriers were prepared. The growth was controlled *in situ* by reflection high-energy electron diffraction (RHEED) indicating well defined streaky pattern characteristic of a 2D growth mode. After growth, *in situ* or *ex situ* annealing of samples was performed. The structural properties of the layers were examined by standard X-ray diffraction (XRD) method revealing in PbTe/CdTe superlattices diffraction satellites up to 7th order (see Fig. 1a). The XRD rocking curve measurement shows high crystal quality of the individual PbTe and CdTe layers — full width at half maximum (FWHM) parameter in the range 124–198 arcsec for CdTe layers and 131–223 arcsec for PbTe layers (on GaAs substrates) was obtained. The cross-sectional observation of the multilayer along growth direction by atomic force microscopy (AFM) (see Fig. 1b) was also employed. The PbTe/CdTe samples

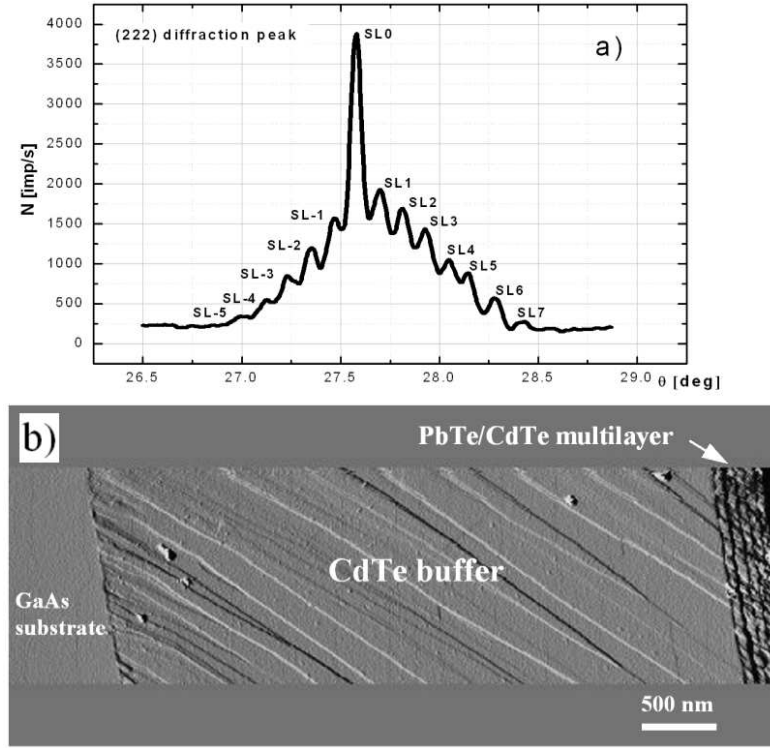


Fig. 1. (a) X-ray diffraction analysis of the crystal structure of $3 \times [\text{PbTe}(12 \text{ nm})/\text{CdTe}(50 \text{ nm})]/\text{CdTe}/\text{GaAs}(001)$ superlattice. SL_i denote the superlattice diffraction peaks of i -th order. (b) AFM image of the cleaved cross-section of the PbTe/CdTe heterostructure grown on (001) GaAs substrate with 4 μm thick CdTe buffer.

were optically characterized at liquid helium (LHe), liquid nitrogen (LN_2) and room temperatures by photoluminescence measurements carried out in backscattering geometry using 1.17 eV line of YAG:Nd pulsed laser for excitation. For this energy the optical excitation occur only in PbTe. For the analysis of luminescence boxcar integrator technique with CdHgTe diode as a detector was used.

3. Optical results and discussion

Figure 2 shows the photoluminescence spectra measured at 4.2 K for PbTe/CdTe heterostructures grown on GaAs substrate with the same 50 nm thick CdTe barriers but different PbTe QW layer thicknesses i.e. 16, 12, and 8 nm. For each sample we observe relatively narrow (except 8 nm QW sample) and well defined photoluminescence (PL) peak with energy between the band gaps of CdTe and PbTe bulk materials. Simultaneously, in agreement with our expectations, the energy of the emission peak shows blue shift with decreasing PbTe well width.

This experimental finding indicates that the observed emission is connected with electron–hole recombination in PbTe quantum wells and the peaks shift is due to quantum size effect.

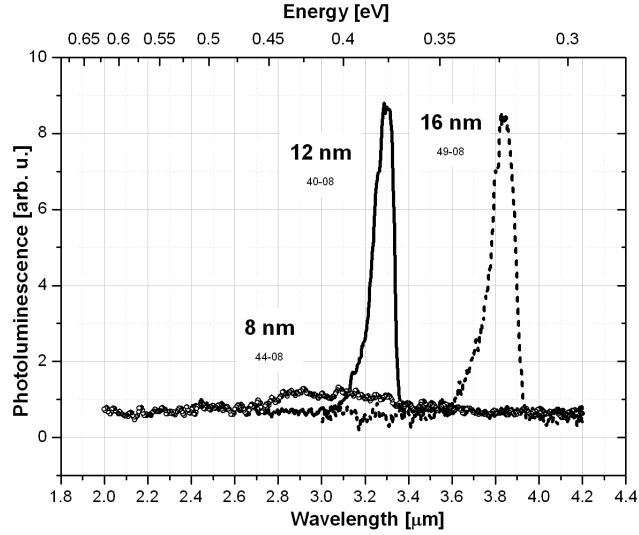


Fig. 2. Photoluminescence spectra of $3 \times [\text{PbTe}(t)/\text{CdTe}(50 \text{ nm})]/\text{CdTe}/\text{GaAs}(001)$ measured at $T = 4.2 \text{ K}$, for different PbTe layer thicknesses t indicated in the figure.

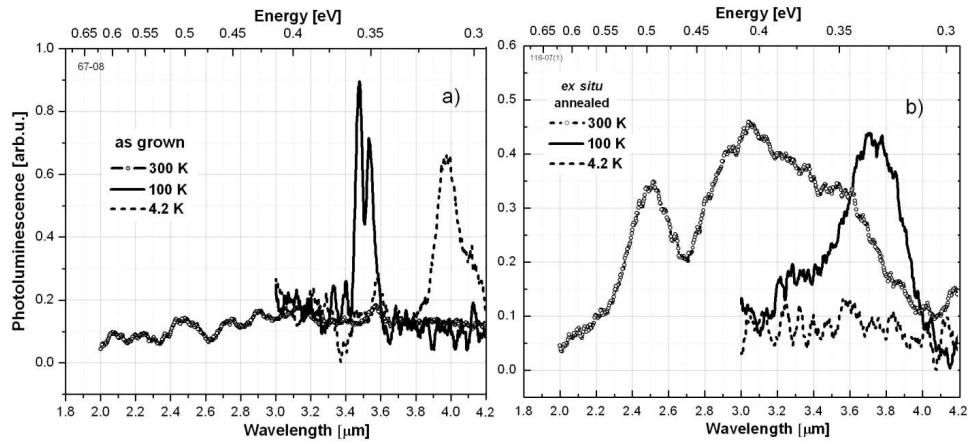


Fig. 3. Photoluminescence spectra of (a) $3 \times [\text{PbTe}(16 \text{ nm})/\text{CdTe}(50 \text{ nm})]/\text{CdTe}/\text{BaF}_2(111)$ as grown layer and (b) $6 \times [\text{PbTe}(8 \text{ nm})/\text{CdTe}(50 \text{ nm})]/\text{CdTe}/\text{BaF}_2(111)$ sample after post growth annealing at 320°C for 10 min.

Figure 3 presents the PL spectra measured at different temperatures (4.2, 100, and 300 K) for two PbTe/CdTe heterostructures grown on BaF_2 substrate.

Photoluminescence spectra for $3 \times [\text{PbTe}(16 \text{ nm})/\text{CdTe}(50 \text{ nm})]/\text{CdTe}/\text{BaF}_2(111)$ as-grown sample are shown in Fig. 3a. In this case, intensive PL peaks are visible in low temperatures ($T = 4.2 \text{ K}$ and $T = 100 \text{ K}$). The temperature coefficient of the PL energy is positive in accordance with that of PbTe gap. This points out that observed mid-infrared emission comes (like in the case of GaAs-deposited structures) from PbTe QW. Another interesting point in Fig. 3a is that observed peaks are composed of two lines, which is clearly visible at $T = 4.2 \text{ K}$. Such line splitting was observed previously in the case of single PbTe/CdTe QW grown on GaAs substrate [1] and was interpreted taking into account the large difference in thermal expansion coefficient of CdTe and PbTe materials: $4.7 \times 10^{-6} \text{ K}^{-1}$ and $20 \times 10^{-6} \text{ K}^{-1}$, respectively [1]. It results in an increase in the lattice mismatch of the PbTe/CdTe up to $\approx 1\%$ below 100 K, and causes the increase in strain in the region of PbTe well. Hence, the double PL peaks can be attributed to the emission from differently strained regions in the well. In the case of $6 \times [\text{PbTe}(8 \text{ nm})/\text{CdTe}(50 \text{ nm})]/\text{CdTe}/\text{BaF}_2(111)$ *ex situ* annealed in vacuum for $t = 10 \text{ min}$ at $T = 320^\circ\text{C}$ (see Fig. 3b), we observe inverse behavior of luminescence in decreasing temperature. Namely, the broad photoluminescence peaks are visible at highest and middle temperatures, but no PL signal at 4.2 K was detected. It is interesting to point out in this place that no photoluminescence was observed for this sample before annealing. The shape of spectrum measured at 300 K is close to the ones recorded previously for PbTe QD samples — obtained by annealing of PbTe/CdTe QW heterostructure grown on GaAs substrate [3, 4]. Thus, we expect that the wide luminescence observed at lower energy is connected to the quantum dots with different spatial sizes, which have arisen as a result of partial decomposition of PbTe layer during annealing. In such interpretation, the narrower line at higher energy correspond to the region of PbTe QW, which did not undergo decomposition. The absence of PL at liquid helium temperature supports such interpretation. It is known from calculations performed by Koike and co-workers [4] that band alignment in the case of PbTe/CdTe QD heterosystem changes from type-I to type-II at temperatures below 120 K (while the QWs system preserves type-I even at low temperatures), which causes the decrease in PL intensity because the indirect transitions are dominant carrier recombination processes in the case of type-II potential. Obviously, more detailed study of PbTe/CdTe//BaF₂ heterosystem are needed for verification of this interpretation.

4. Conclusions

MBE growth optimization and optical properties of the lattice-type mismatched PbTe/CdTe heterostructures on GaAs and BaF₂ substrates were reported. The XRD measurements confirm high crystal and structural quality of obtained structures. High efficiency PL was observed in the infrared region from PbTe quantum wells grown on GaAs(001) as well as on BaF₂(111) substrates. The increase in the luminescence energy with the decreasing PbTe layer thickness was

clearly observed and discussed in terms of quantum size effect. For PbTe/CdTe heterostructures grown on BaF₂ substrate strong influence of post-growth annealing on luminescence was found indicating the transformation of PbTe wells into an assembly of PbTe dots.

Acknowledgments

This work was supported by the research project No. 0992/T02/2007/32 granted by Ministry of Science and Higher Education (Poland) for the period 2007–2010.

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