Semiconductor Physics, Quantum Electronics & Optoelectronics, 2006. V. 9, N 4. P. 31-35.

PACS 43.35.+d, 73.61.Ga, 73.50.Jt

Layered structure formation in $Hg_{1-x}Cd_xTe$ films after high-frequency sonication

R.K. Savkina, F.F. Sizov, A.B. Smirnov, V.V. Tetyorkin
V. Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine
41, prospect Nauky, 03028 Kyiv, Ukraine
Phone:(044) 525-1813, fax: (044) 525 1810
r_savkina@rambler.ru; sizov@isp.kiev.ua; alex_tenet@isp.kiev.ua

Abstract. Electrophysical parameters of $Hg_{1-x}Cd_xTe$ thin films grown by liquid-phase epitaxy and molecular-beam epitaxy were investigated before and after the high-frequency sonication (f_{US} = 7.5 MHz, $W_{US} \sim 10^4$ W/m^2). It was determined that parameters of MBE-grown $Hg_{1-x}Cd_xTe$ thin films are stable to ultrasound effect, while for thin films grown by LPE the sonically stimulated change of the conductivity type was observed. The best agreement between experiment and calculation was obtained in the frame of the assumption about forming of the thin layer with another conductivity type. The possible nature of the observed effect was analyzed.

Keywords: $Hg_{1-x}Cd_xTe$ thin films, sonication.

Manuscript received 19.10.06; accepted for publication 23.10.06.

1. Introduction

Solid solutions $Hg_{1-x}Cd_xTe$ (MCT) have important technological application for infrared devices despite numerous attempts to replace it with alternative materials. This follows both from fundamental considerations and the material flexibility. At present efforts in infrared detector research are directed towards improving the performance of single element devices, large electronically scanned arrays and higher operating temperature [1-3]. At the same time, stability of electrical parameters of MCT epitaxial layers under the external actions is an important factor of reliability of the infrared FPA detector.

It is known that MCT is very soft and brittle material; defects can be easily introduced during preparation processes as well as by handling. The quality of MCT based devices can be dramatically changed as a result of the degradation process connected with an action of external factors (deformation, temperature, irradiation), which give rise to active transformation of the defect system in this material.

We suppose that the high-frequency ultrasound (US) is a good tool for driving the material into the non-equilibrium state and transformation of the defect system. Acoustic-wave treatment, to some extent, simulates the processes of degradation, producing the condition to study the stability of the layer parameters in a relatively short time interval. In this work, we have investigated the electrophysical parameters of MCT thin films before and after sonication to determine changes of the carrier transport stimulated by the high-frequency and high-intensity deformation.

2. Experiment

MCT thin films (x~0.2) for 8…12 μm spectral region FPAs were grown by liquid-phase epitaxy (LPE) and molecular-beam epitaxy (MBE) methods. MBE-grown MCT epitaxial layers were grown on the 2-inch-diameter (013) GaAs substrates with an intermediate CdZnTe buffer layer. The as-grown layers were of *n*-type conductivity, and *p*-type MCT layers were obtained by annealing at 200–300 °C. Semi-insulating CdZnTe plates were used as a substrate for LPE-grown *p*-type MCT layers. The thickness of grown layers was about 10…20 μm.

The sonication of MCT thin film samples was carried out with the aid of the $LiNbO_3$ piezo-transducer at the frequency f_{US} = 7.5MHz. Longitudinal vibrations with the intensity $W_{US} \sim 10^4$ W/m^2 were excited. The treatment time amounted to 30 min at room temperature.

The concentration and mobility of free carriers in MCT layers were determined from the Hall coefficient R_H and conductivity σ measurements which were made by van der Pauw method at $T = 78$ K and magnetic field $B = 0…0.7$ T. Samples 1×1 cm in size were cut from wafers for measurements. The high resistivity of the substrates excluded any influence on the results of electrical measurements. A standard procedure of the photoconductivity spectroscopy was also used before and after the sonication.

3. Results

The change of the measurable parameters after sonication was observed for all the samples. Figs 1 and 2 show typical field dependences of the Hall coefficient for investigated MCT films. Points in figures represent the experimental Hall effect data, and solid lines are the results of the fitting procedure. The Hall effect data were processed in terms of the model including several kinds of carriers using the following expression [4]:

$$eR_H(B) = \frac{\sum a_i \mu_i c_i(B)}{\left(\sum c_i(B)\right)^2 + B^2 \left(\sum a_i \mu_i c_i(B)\right)^2}, \tag{1}$$

where e is the electric charge, $c_i = n_i\mu_i/(1+\mu_i^2B^2)$, n_i is the concentration of the i-th type of carrier, μ_i is the mobility of the i-th type of carrier, a_i is the sign of carrier (−1 for electrons, +1 for holes), and B is the magnetic induction. In addition, the zero magnetic field electrical conductivity is given by $\Sigma(0) = e\Sigma c_i(0)$. The electron and hole concentration and mobility were obtained before and after US treatment.

In MBE-grown *p*-type MCT layers, the initial values of the Hall coefficient R_H and conductivity σ are independent of the magnetic field induction B. This indicates that only carriers of a single kind are present. After sonication, a moderate increase of the hole concentration and the mobility decrease were observed (see the Table 1, sample 1).

In MBE-grown *n*-type MCT layers, the initial value of the Hall coefficient R_H is dependent on the magnetic field B (see Fig. 1). Attempts to describe the experimental data, using one carrier type (electron) or combined electron and hole conductivities and also taking into account the light hole contribution, were equally unsuccessful. The Hall effect data were satisfactorily explained by using two types of electrons of significantly different mobility and concentration as well as considering the field dependence of the conductivity $\sigma(B)$. Moreover, the best agreement between experimental and calculated $R_H(B)$ dependences is obtained if suppose an existence of the layer with heavy electrons. The calculated values of the layer characteristic dimension d_{layer} and charge carrier parameters for one of samples are shown in Table 1 (sample 2). After sonication, a tendency to the electron concentration increase and the mobility decrease is observed.

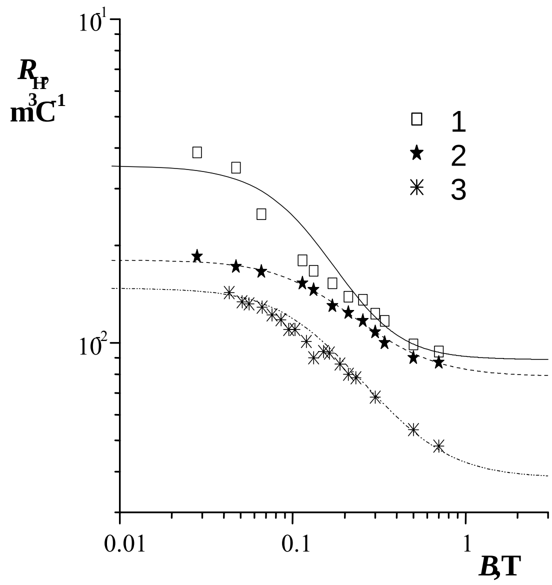

Fig. 1. Magnetic field dependences of the Hall coefficient for the typical MBE-grown *n*-type $Hg_{1-x}Cd_xTe$ layer. Curve 1 – initial data; curves 2, 3 – after second sonication and in two years storage, respectively.

The initial field dependence of the Hall coefficient of the typical LPE-grown *p*-type MCT layer is shown in Fig. 2 (curve 1). Concentration and mobility of majority carriers for this sample are presented in Table 2. After sonication, the change of the conductivity type $p\to n$ at low magnetic field took place (see Fig. 2, curve 2). Fitting procedure to the experimental data was applied in this case, too. The best agreement between the experimental and calculated $R_H(B)$ dependences was obtained within the framework of the assumption about ultrasonically stimulated formation of the layer with *n*-type conductivity. The layer characteristic dimension d_{layer} and charge carrier parameters were determined (see Table 2).

4. Discussion

Thus, we demonstrated that the action of the acoustic wave excited in MCT epilayers by piezo-transducer results in a change of the carrier concentration up to the change of the conduction type.

4.1. Stability of parameters describing MCT thin films

Experimental data from Tables clearly show that parameters of MCT thin films grown by MBE are more stable to sonication than those of films grown by LPE. For MBE samples, a noticeable change of the charge carrier mobility and concentration took place after the second US treatment only. It should be also noted the radiation hardness both MBE-grown MCT films [5] and photodiodes prepared by using similar MCT films [6].

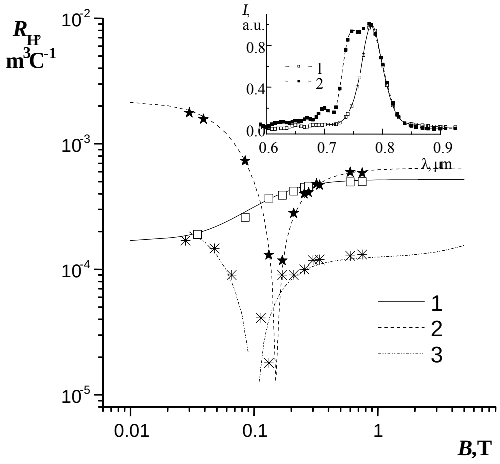

Fig. 2. Magnetic field dependences of the Hall coefficient for the typical LPE-grown *p*-type $Hg_{1-x}Cd_xTe$ layer. Curve 1 – initial data; curves 2, 3 –after first and second sonication, respectively.
Inset. Normalized curves of the photocurrent spectral response of $Cd_{1-x}Zn_xTe$ substrate before (1) and after (2) sonication, $T = 78$ K.

First of all, it could be connected with growth features. Among the various epitaxial techniques, LPE and MBE are the most often used methods, enabling growth of device-quality homogeneous layers and multilayered structures [1]. But MBE growth is carried out at lowest temperatures (160…200 °C) as compared with 450 °C for LPE. Remaining problems of LPE are frequent occurrences of a terraced surface morphology, sharpness of the interface region and a relatively high density of misfit and threading dislocations. The reduction of the growth temperature precludes impurity diffusion from the substrate into MCT films resulting in reduction of the background doping down to 1–1.5 order at the same purity of material for MBE synthesis [7].

The degree of the structural perfection of MCT films is also very important factor. The structural perfection of the epilayer strongly depends on the conformity between parameters of substrate and layer. It is now widely acknowledged that substrates are a major limiting factor in uniformity and reproducibility of MCT detector arrays. At first sight, the highest crystal perfection is realized for MCT layers on lattice matched CdZnTe substrates in contrast to the high defect density generation due to a large lattice mismatch for MCT layers on GaAs substrates. As determined by the etch pit density method, the dislocation density in MBE-grown MCT films was about 10^6 cm^{-2}. In LPE-grown MCT films this value did not exceed 10^5 cm^{-2}. Hence, they should be more stable to US influence in accordance with a phenomenon of the correlation between the degree of the structural perfection and the value of the sonically stimulated effect observed for bulk MCT crystals [8].

Table 1. Some parameters of typical investigated $Hg_{1-x}Cd_xTe$ epilayers grown by MBE, T = 78 K. Parameters n_d and μ_d are the concentration and mobility of "heavy" electrons.

Sample	p, n, cm^{-3}	μ_p, μ_n, cm^2/V·s	n_d, cm^{-3}	μ_d, cm^2/V·s	d layer, μm	ρ, Ohm·cm	
1. x=0.22 d=12 μm	$8\cdot10^{15}$ $9\cdot10^{15}$ $16\cdot10^{15}$	373 360 247	– –	– – –	– – –	2.1 1.9 1.56	Initial 1st sonication 2nd sonication
2. x=0.21 d=14 μm	$2.3\cdot10^{13}$ $2.3\cdot10^{13}$ $2.5\cdot10^{13}$	84500 84500 70000	$1.8\cdot10^{15}$ $1.8\cdot10^{15}$ $2.1\cdot10^{15}$	8000 8000 5800	1.5 1.5 2.8	1.87 1.85 1.6	Initial 1st sonication 2nd sonication

Table 2. Some parameters of typical investigated $Hg_{1-x}Cd_xTe$ epilayers grown by LPE, T=78 K. Parameters n_d and μ_{nd} are the same as in Table 1.

Sample, x=0.2 d=19μm	P, cm^{-3}	μ_p, cm^2/V·s	n, cm^{-3}	μ_n, cm^2/V·s	n_d, cm^{-3}	μ_{nd}, cm^2/V·s	d_{layer}, μm	ρ, Ohm·cm
Initial 1st sonication 2nd sonication	$1.2\cdot10^{16}$ $1.1\cdot10^{16}$ $3.5\cdot10^{16}$	511 320 222	$3\cdot10^{11}$ $3.3\cdot10^{11}$ 10^{11}	85000 120000 140000	– $2\cdot10^{14}$ $3\cdot10^{15}$	– 1000 1000	– 2.28 4.8	0.89 1.6 0.54

But it seems that other factor plays key role here. The wavelength of ultrasonic applied in our experiment amounts to 400…700 μm and exceeds the thickness of grown layers essentially. In other words, the wave propagation process takes place in the substrate. Hence, it could be expected that sonically stimulated phenomena in epilayers are determined by sonically stimulated processes at the substrate.

It is obvious that the photocurrent is a very sensitive parameter to the composition and the state of the point and extended defect system in a semiconductor crystal. We have investigated the spectral response of the photocurrent both for MBE-grown and for LPE-grown structures illuminated from the substrate side before and after sonication. We also controlled the photosensitivity value of MCT thin films.

The US effect on the photocurrent spectral response of the GaAs substrate was insignificant. At the same time, the sonication of the CdZnTe substrate has resulted in the photosensitivity increase and the change of the spectral distribution of the photocurrent (see inset in Fig. 2). The fact of a better stability for an external action of GaAs substrate parameters in comparison with parameters of CdZnTe substrates could be connected with the larger stacking fault energy and the smaller ionicity of III-V compounds compared to II-VI ones. It is also necessary to note, that the photosensitivity of the MBE MCT epilayers was increased slightly – by a factor of two, while an essential rise of the photosensitivity of LPE-grown *p*-type MCT layers took place after sonication.

Let us consider the sonication influence on photocurrent spectra of CdZnTe substrate. The initial spectrum is a selective peak with the spectral position of the "red" edge, which corresponds to the bandgap E_g = 1.53 eV (x = 0.04). It was used a relation between the bandgap of $Cd_{1-x}Zn_xTe$ compounds and x [9]:

$$E_g(x) = 1.5045 + 0.631x + 0.128x^2. \quad (2)$$

After sonication, the structure of the photocurrent spectrum has changed. Data from inset in Fig. 2 clearly shows that the "red" boundary does not change position and additional energy peak emerges. Such "broadening" of the initial peak after sonication is likely to be associated with macro-inhomogeneity of the solid solution and formation of $Cd_{1-x}Zn_xTe$ mixed structure with variable bandgap between 1.53 and 1.6 eV (x = 0.04…0.16).

Recently, we have determined (by the example of $Cd_{1-x}Mn_xTe$ [10]) that the energy transferred by the elastic wave is sufficient for the beginning of the point defect structure transformation that has resulted in the crystal photosensitivity increasing. We have suggested that the photosensitivity increase after the sonication of $Cd_{1-x}Zn_xTe$ substrate could be associated with the generation and the following diffusion of vacancies, which are acceptors and centers of photosensitivity for CdTe and CdTe-based alloys [11]. It is also well known that in the A_2B_6 semiconductor compounds zinc has an intrinsic tendency to form not only substitutional defects but also interstitials. Interstitial zinc that is a mobile donor defect usually associates in clusters and precipitates at various kinds of macrodefects in the crystal (dislocations, grain boundaries and twins) [12]. One can assume that sonically stimulated cluster dissociation and escape of zinc from sinks can be responsible for the formation of CdZnTe compound with bigger composition in comparison with matrix. On the other hand, the change of epilayer properties is possible in the issue of zinc diffusion from the substrate. As has been shown in [13], acoustic wave treatment stimulates the out-diffusion of mobile defects from the CdTe substrate in *p*-type CdTe MOCVD epilayers.

Thus, the above results allow making the preliminary conclusion about a significant role of the substrate type for the stability of the MCT epilayers. Let us now consider processes taking place in the epilayer directly.

4.2. Carrier concentration change in MCT thin films

As it was noted previously, immediately after growth MBE-grown MCT layers are *n*-type; *p*-type MCT layers are obtained by the annealing in consequence of the mercury diffusion from the volume, which remains doped by acceptor-like Hg^- vacancies. Evidently, the similar process occurs during a sonication also as a result of the local heat release due to the absorption of US vibration [14] and the decrease of the ion diffusion activation energy [15]. It could be resulting in the increase of holes concentration both for MBE, and for LPE MCT films. The ultrasonic effect is similar to the process of the natural degradation of MCT in this case.

The sonically stimulated change of the electron concentration takes place mainly at the expense of the change of the contribution of low-mobility ("heavy") electrons (see Tables). Calculation has shown that heavy electrons are presented in the initial MBE-grown *n*-type MCT layers. In LPE-grown *p*-type MCT layers they appear after the first US treatment. After the second sonication, their contribution (the value of the characteristic dimension d_{1layer}) increases in both cases. It is necessary to note also that the concentration of "heavy" electrons exceeds considerably the concentration of "light" electrons.

Heavy electrons are observed both in MCT bulk crystals [16] and in films grown by LPE [17] and MBE [18]. But the reasons for their appearance are not always clear. Thus, low-mobility electrons may be present for the reason of the conduction band bottom modulation, due to random distribution of electrically charged centers giving rise to density-of-states tails, or as a consequence of the enriched layers at the surface. A study of galvanomagnetic phenomena in MBE-grown *n*-MCT films has shown that the most probable sources of such electrons are surface layers and electrical microheterogeneities [19]. As shown in [19], various surface treatments affect the parameters of low-mobility electrons. For example, the anodic oxide deposited onto the MCT film surface makes the concentration of low-mobility electrons higher and that of anodic fluoride lower. At the same time, it is necessary to consider the formation of regions in the bulk, in which the electron mobility is lower for some reason. The inclusion boundaries may well be regions of this kind.

Considering the prevalence of the sonic-dislocation mechanism of the interaction between ultrasonic wave and crystal [20], we suggest that dislocations including ambient atmosphere of impurities and intrinsic defects could be considered as such inclusions with regions of low-mobility electrons around them. Especially since the dislocation presence has resulted in the conduction band bottom modulation also. It is necessary to remind that the best agreement between measured and calculated $R_H(B)$ dependences for LPE-grown *p*-type and MBE-grown *n*-type MCT layers is obtained if suppose an existence of the conducting binding layer with "heavy" electrons. The increase of the characteristic dimension of this channel after the sonication could be connected with redistribution in dislocation atmospheres as well as with a sonically stimulated generation of new dislocations.

5. Conclusion

Thus, the change of electrophysical parameters of MCT thin films as a consequence of the ultrasonic influence was investigated. We have demonstrated that the action of the acoustic wave excited in MCT epilayers by piezo-transducer results in a change of the charge carrier concentration up to the conductivity type conversion. The best agreement between experiment and calculation is obtained if suppose a sonically stimulated formation of the layer with an alternative conductivity.

It was also determined that parameters of HgCdTe/CdZnTe/GaAs heterostructures grown by MBE are more stable to the high-frequency and high-intensity elastic deformation effect than HgCdTe/CdZnTe heterostructures grown by LPE. Substrate properties have been observed to play a significant role for the stability of the heterostructure.

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