$Zn_xCd_yHg_{1-x-y}Te$ solid solutions – an alternative material for infrared devices

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1. Introduction

$Cd_xHg_{1-x}Te$ (MCT) solid solutions are a base material for infrared devises. However, it is a well-known fact that they have a considerable defect – weak mercury-tellurien bond. This leads to the decrease of dislocation energy, vacancy formation energy, and as result – to the low hardness and instability of properties. This weakness of mercury-tellurium bond is caused not only by correlated term value of these atoms. In the paper of A. Sher et al. [1] it was shown that it is just CdTe that destabilizes HgTe bond in solid solution. In Table 1 the correlated therm values of atoms are leasted, which are components of solid solution and corresponding bond energies of three compounds. The experimental bond length, polarity and metallic contribution to the bond energy are also plotted. The valence and states energies for Zn are large, but becomes smaller for Cd, and are deeper again for Hg. At the same time the bond length and polarity for CdTe bond are larger, while the ZnTe bond length is shorter. In [1] it have been also calculated the bond length and energies for different configurations CdHgTe in alloys for example: Cd(1)Hg(3). The unexpected result was obtained: the shorter HgTe bond becomes still shorter in the alloy while the CdTe bond length increases. The already weak HgTe bond is destabilized by the presence of Cd. The difference between Zn and Cd occurs because in the Cd case there is a net transfer of electrons from the Cd to the Hg, while in the case of Zn there is no such transfer. There extra transferred electrons must occupy antibonding states, because the bonding states on HgTe are full. That results in destabilization of the HgTe bonds. Zn in ZnCdHgTe (ZMCT) solid solution will serve the stabilizing function in two ways. The first is that Zn stabilizes weaker bonds in alloys and accordingly vacancy formation energies in alloys should be larger than those in the pure constituent CdTe or HgTe. The second effect is following: the shorter bond lengths of the ZnTe will increase the dislocation energies. Those should inhibit dislocation loop formation and increased hardness. ZnCdHgTe may be superior to CdHgTe for infrared devices.

In this work we consider the energy-band structure and phonon spectra peculiarities ZnCdHgTe of solid solution on the basis of the data of previous papers [2] and [3] as well as new results.

2. The general characteristic of solid solutions

The composition diagram of ZnCdHgTe solid-solutions is presented in Fig. 1. Since we deal with alloys of three constituents: HgTe, CdTe and ZnTe, we have a composite

Table 1. **Correlated term values and bond energies for three II-VI compounds. The experimental bond lengths polarity and metalic contribution to the bond energy are also plotted** [1]

Atom	Correlated term values [eV] s	p	sp^3
Zn	−10.224	−4.920	−6.246
Cd	− 9.611	−4.784	−5.991
Hg	−10.946	−4.872	−6.391
Te	−19.620	−9.824	−12.273

Compound	Bond energies d(Å)	a_p	$E_{metalic}$ [eV]	E_b [eV]
ZnTe	2.643	0.652	−0.625	−0.985
CdTe	2.805	0.710	−0.466	−0.944
HgTe	2.797	0.685	−0.614	−0.480

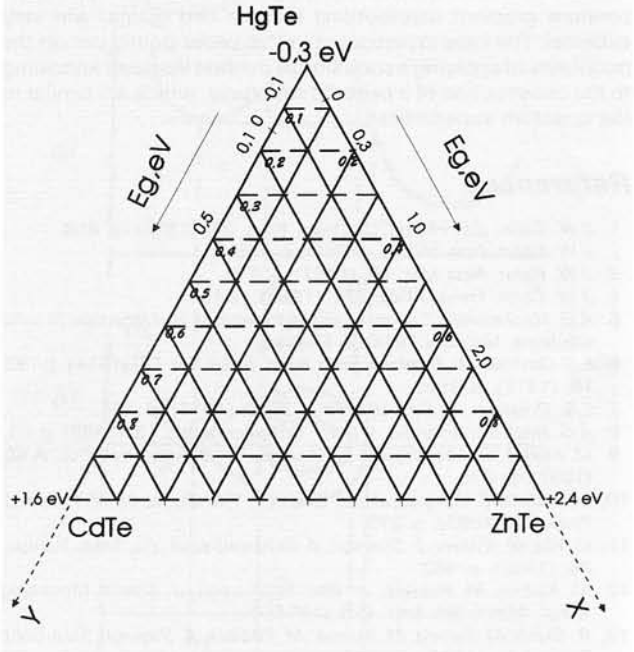

Fig. 1. Composition diagram of ZnCdHgTe solid-solutions

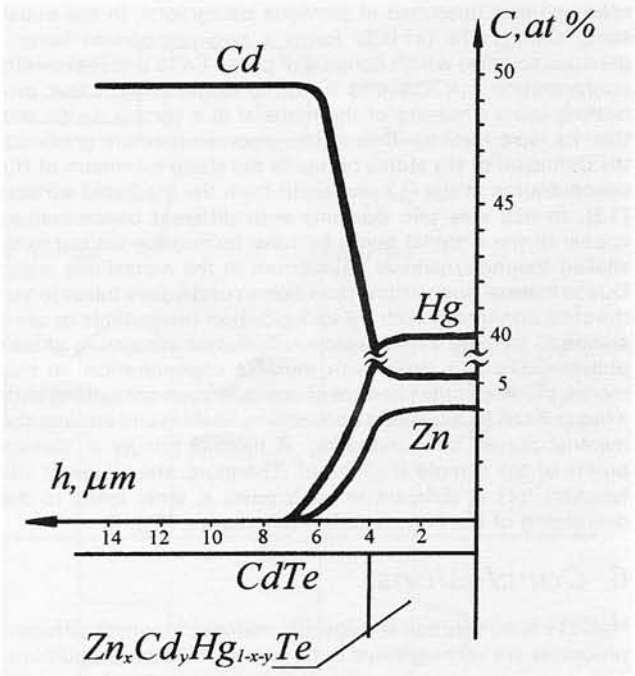

Fig. 2. Deep profils of sample I

Table 2. **Data of the specimens $Zn_xCd_yHg_{1-x-y}$**

	$\lambda_{1/2}$ [μm]	x	y	n [cm^{-3}]	μ [cm^2/V]
Sample I	6.9	0.09	0.08	$4\cdot10^{15}$	$9\cdot10^4$
Sample II	4	0.12	0.10	$5\cdot10^{15}$	$5\cdot10^4$
Sample III	3.6	0.17	0.07	$2\cdot10^{15}$	$2\cdot10^4$

triangle. The point inside this triangle show the composition of four component solid solutions. The sides are the diagrams of respective three component solid solutions. The changes of energy gaps for CdHgTe and ZnHgTe alloys are shown on the left and right of the two sides. For the former we have zero energy gap at fifteen percent of CdTe and the later at eight percent of ZnTe. It means that the important compositions for infrared devices are placed in the upper angle of composite diagram. (The HgTe energy gap is minus 0.3 eV, for CdTe and ZnTe energy gaps are 1.4 eV and 2.4 eV, accordingly).

We study the epitaxial films of ZnCdHgTe alloys obtained by liquid phase epitaxy on CdTe substrates. The parameters of three layers of $Zn_xCd_yHg_{1-x-y}Te$ alloys, which was used in cyclotron resonance and magnetophonon resonance experiments, are listed in Table 2. As shown by X-ray microanalysis (see the deep profile on Fig. 2) the thickness of homogeneous layer was near 4 μm. It is seen that the quality of epitaxial layers are comparing with $Cd_xHg_{1-x}Te$ alloys with the same energy gap (near 180÷300 meV). The mobility of elections in these layers is sufficiently high, in consequence of which the cyclotron and magnetophonon resonance we were able to observe. It is necessary to note that parameters of these samples did not change during three years.

3. Peculiarities of energy-band structure parameters

The energy-band structure was studied by means of magnetophonon and cyclotron resonances. Second derivation of transverse magnetoresistance $\partial^2\rho_{xx}/\partial B^2$ as a function of magnetic field B was registered up to 6.5 T at different temperatures in the range 77÷200 K. Cyclotron resonance has been studied using the technique of the changes in photoconductivity in magnetic field up to 6.5 T at 4.2 K under radiation.

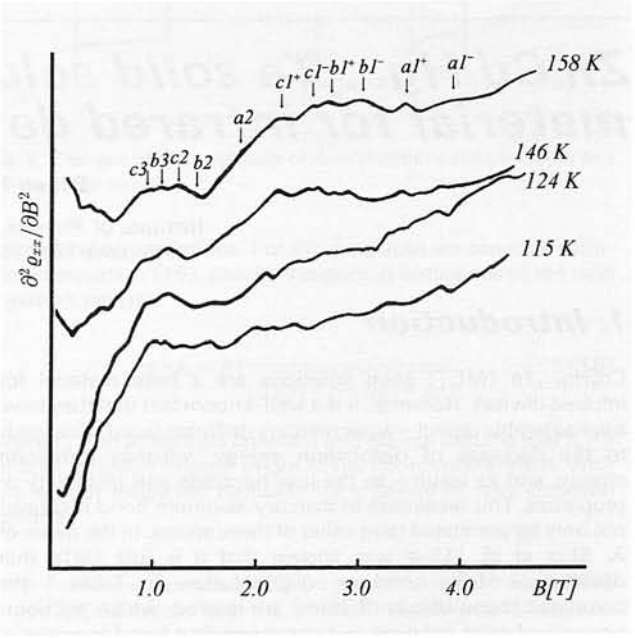

Fig. 3. Experimental plots of for sample I

The experimental plots of $\partial^2\rho_{xx}/\partial B^2$ for sample I measured at four different temperatures are shown in Fig. 3. When the temperature increases above 124 K, a group of strong peaks appears in the range from 2.0 to 3.0 T, to which their harmonics correspond at 1.0÷1.5 T and 0.4÷0.7 T. These three series of peaks a, b, c, can be interpreted as ordinary magnetophonon resonance (MPR) with the participation of LO phonons of ZnTe-like, CdTe-like and HgTe-like lattices, respectively. The strongest and the most distinguishable at $T>124$ K peak (1c) provided by absorption of LO phonon in HgTe-like lattice due to the transition from 0^+ Landau level to 1^+ was used for determination of the band structure parameters under the first approximation, since the energy of LO(HgTe) phonon for solid solution MCT is known and hardly changes [4] with the composition of Cd (probability of Zn also for $x+y<0.3$ in ZMCT). Spectra of photoconductivity of specimen III for different wavelengths have been shown in Fig. 4. In spectra one

bright line can be noticed. Extrapolation to $B=0$ shows that in the given case we observe transitions of intraband conductivity.

The energy gap was estimated in first approximation corresponding to photoluminescence data [5]. Band structure parameters were calculated according to the Pidgeon-Brown model [6] in R. R. Aggarwals [7] version. The experience of authors [8, 9] for determination of the band structures parameters in MCT was used when values for γ_1^L, γ_2^L, γ_3^L, K^L and F parameters were chosen. Therefore we take the following:

$$\gamma_1^L = \frac{E_p}{3E_g} + 2.5,$$

$$\gamma_2^L = \gamma_3^L = \frac{E_p}{6E_g}.$$

We assumed that $E_p = 17.9$ eV and $\Delta = 1.0$ eV [8] and they do not depend on temperature and composition [8]. For other parameters, according to [10]:

$$K = \gamma_3 - \frac{1}{3}\gamma_1 + \frac{2}{3}\gamma_2 - \frac{2}{3} - \frac{5}{4}\delta_{exch}$$

Here δ_{exch} is the correction caused by the nonlocality of potential and equal to 0.4 for MCT [10] and for F we refer to the value determined by Weiler et al. [8], therefore F= −0.5. Having obtained band parameters in this manner, a correction was done by best fit procedure to the experimentally obtained positions of peaks in series c^+, c^- – MPR with the participation of LO(HgTe)-phonon with transitions from 0^{+-} levels to 1^{+-}, 2^{+-} Landau levels. Band parameters obtained in this way have been presented in Table 3 (T=77 K). Temperature dependence of E_g (T) and m_e (T) calculated with the help of the temperature shift of MPR peaks and from data of cyclotron resonance (for sample III) are shown in Fig. 5. The value of the coefficient dE_g/dT (equal to 0.136 meV/K for sample I and 0.11 meV/K for sample III) was obtained from the dependence of $E_g(T)$ in Fig. 5. It is smaller than that calculated with the use of the temperature shift of the photoluminescence band (0.18 meV/K for sample III).

The temperature dependence of E_g (T) and m_e (T) for sample I are the like to ones for $Cd_{0.196}Hg_{0.804}Te$ [11] but it is shown from Fig. 5 that increasing of addition of Zn leads to decreasing of the temperature dependence of the band-structure parameters. That can allow to obtain so composition of $Zn_xCd_yHg_{1-x-y}Te$ alloys with not depending on temperature band-structure parameters. It is assumed that the effective mass of heavy holes equal to $m_{hh} = (\gamma_1 - 2\gamma_2)^{-1}$ does not depend on temperature, which agrees with the experiment for CdHgTe [8] and InSb [12].

Table 3. **Band-structure parameters**

Specimens	E_g [eV]	E_p [eV]	γ_1	$\gamma_2=\gamma_3$	K	F
I	0.18	17.9	35.65	16.55	14.53	0
II	0.31	17.9	21.75	9.6	7.58	−0.2
III	0.35	17.9	19.55	8.5	6.48	−0.5

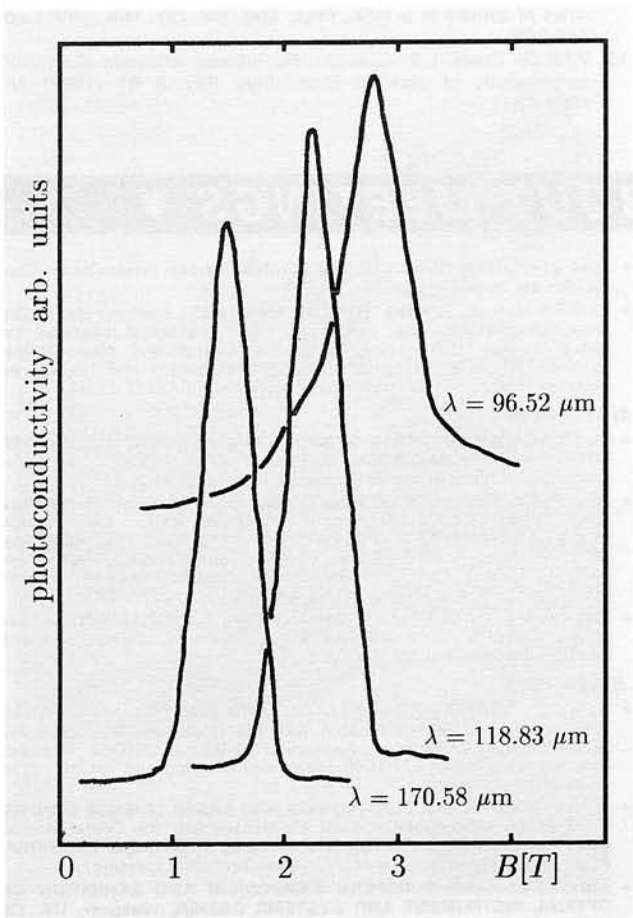

Fig. 4. Spectra of photoconductivity of specimen III

4. Peculiarities of phonon-spectra

As was assumed from data of magnetophonon resonance, ZnCdHgTe solid solutions have three mode behavior of the phonon spectra. With an aim to confirm this assumption the reststrahlen spectra of $Zn_xCd_yHg_{1-x-y}Te$ were measured. The far-infrared reflection-absorption spectroscopy of thin film [13] was used in this experiment. The curve of the reflection-absorption absorbance is shown in Fig. 6 for the epitaxial film $Zn_{0.07}Cd_{0.2}Hg_{0.73}Te$. In spectrum five bright lines can be noticed: at 143 cm^{-1}, 153 cm^{-1}, 165 cm^{-1}, 176 cm^{-1} and 193 cm^{-1}. It can be assumed that the last two lines are connected with ZnTe-like lattice and two middle lines at 153 cm^{-1} and 165 cm^{-1} correspond to CdTe-like lattice. Only one line – at 143 cm^{-1}, can be connected with HgTe-like lattice. This spectrum give the evidence of the three mode nature of the phonon spectra of ZnCdHgTe solid solutions.

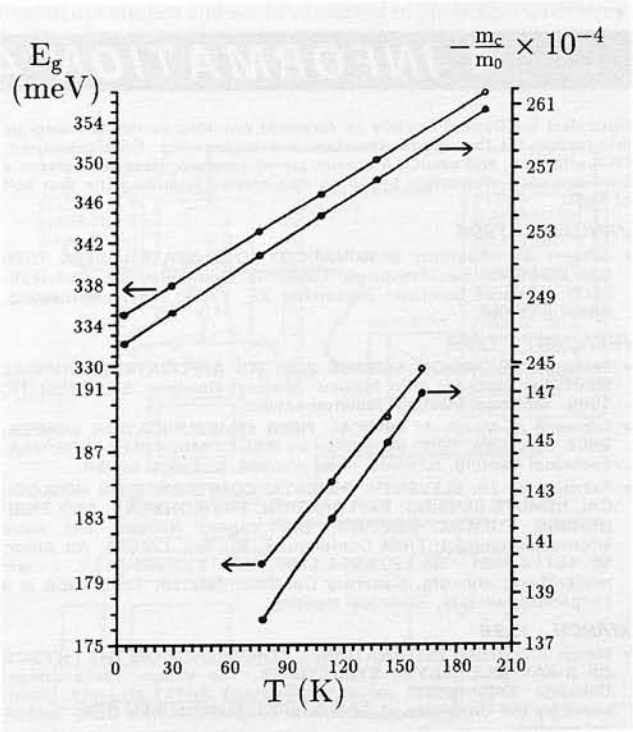

Fig. 5. Temperature dependence of energy gab E_g (T) and electron effective mass on edge of conduction band m_e (T) for sample III – upper curves

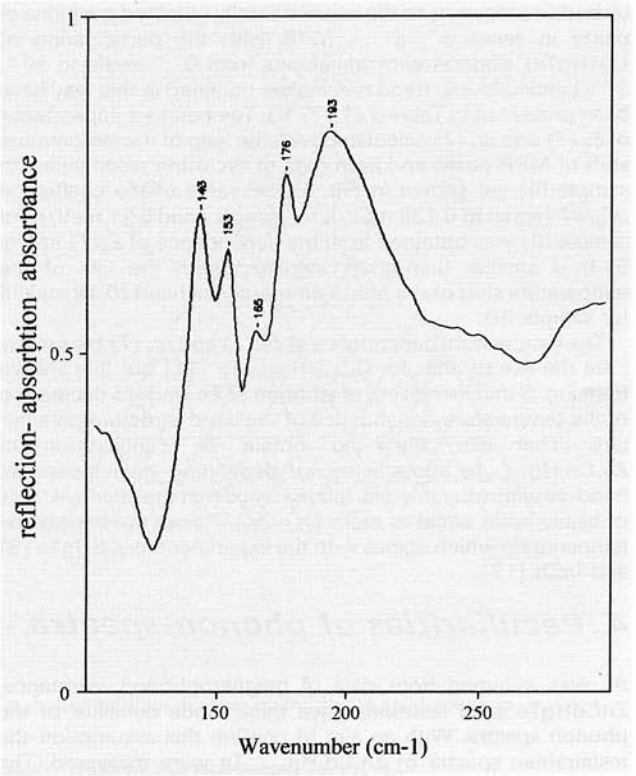

Fig. 6. Reflection-absorption absorbance for $Zn_{0.07}Cd_{0.20}Hg_{0.73}Te$ solid solution

5. Conclusions

- Zn stabilizes the weaker bond in ZnCdHgTe alloys.
- The parameters of epitaxial layers of $Zn_xCd_yHg_{1-x-y}Te$ alloys are comparing with ones of $Cd_xHg_{1-x}Te$ alloys and unchanging for three years.
- The two unique property (as for as known) have ZnCdHgTe alloys:
  - it is possible to obtain the solid solutions $Zn_xCd_yHg_{1-x-y}Te$ with not depending on temperature band-structure parameters;
  - the three mode behavior of phonon spectra.

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