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Growing Cd$_{1-x-y}$Mn$_y$Hg$_x$Te single crystals and their optoelectronic properties

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Abstract. Single crystals of Cd$_{1-x-y}$Mn$_y$Hg$_x$Te:V ($x = 0.05$; $y = 0.03$–0.07, $N_V = 1 \cdot 10^{19}$ cm^{-3}) have been grown and their electrical and optical properties have been studied. The transmission spectra of the samples with the composition $x = 0.05$; $y = 0.07$ were characterized by the minimum in the 3.5–5.5 μm spectral range. In order to understand the nature of it the energy diagram of vanadium levels has been considered. The band gap of the studied solid solutions with different manganese content has been found from the absorption coefficient spectra and compared with those calculated.

Keywords: manganese, Bridgman method, semi-imsulating materials, transmission, band gap.

Quaternary solid solutions of Cd$_{1-x-y}$Mn$_y$Hg$_x$Te, Cd$_{1-x-y}$Mn$_y$Hg$_x$Se prove to be prospective materials sensitive to the external influence, i.e. magnetic and electric fields, pressure, impurities etc. Comparing to the analogous ternary solid solutions, the following features are typical of the named materials:

(I) a stronger bound of Hg atoms with those of crystalline lattice;

(II) significant effect of temperature and external magnetic field on the physical properties;

(III) a possibility of the bang gap tailoring through the independent variation of the manganese or cadmium content as well as a values of exchange contributions can be modified altering the composition of a magnetic component

At the present stage a considerable number of scientific papers are dedicated to investigation of the quaternary semimagnetic semiconductors, such as Cd$_{1-x-y}$Mn$_y$Hg$_x$Te, with a large mercury content. This is due to their possible application in photoreceivers, which operate in the 8–14 μm spectral range and possess more stable characteristics by comparison with Cd$_x$Hg$_{1-x}$Te [1–9]. Investigations of Cd$_{1-x-y}$Mn$_y$Hg$_x$Te with the band gap close to that of cadmium telluride are urged by the practical interest of their use in a character of highly sensitive photorefractive materials for the near IR, where up-to-date optical communication lines operate and the most efficient solid state lasers irradiate.

Although growth and characterization of CdTe:3d are the objects of a great deal of researches, e.g. [10–12],

one of the key problems in the way of device fabrication on its base remains to be the obtaining of the highly sensitive crystals with stable parameters.

The aim of the given paper is to obtain vanadium doped single crystals of Cd$_{1-x-y}$Mn$_y$Hg$_x$Te with compositions of $x = 0.05$; $y = 0.03$–0.07, $N_V = 1 \cdot 10^{19}$ cm^{-3}, and to study their electrical and optical properties.

Single crystals of Cd$_{1-x-y}$Mn$_y$Hg$_x$Te ($x = 0.05$; $y = 0.03$–0.07) were grown via vertical Bridgman method. Temperature gradient on the crystallization front amounted to 15 K/cm and the growth rate was approximately 2 mm/hour.

Zone rectified tellurium and cadmium were used as starting materials. A content of electrically active impurities along the whole length of zone rectified tellurium was controlled through the measurement of the effective value of Hall coefficient. Their concentration was found to fall within the range from $(6–8) \cdot 10^{14}$ cm^{-3} to $(1–2) \cdot 10^{15}$ cm^{-3}. Cadmium purification was performed by the molten zone method in the graphite-covered containers in the ambience of hydrogen. The purity grade of manganese after vacuum distillation was of 9.999. The P^6 mercury of industrial purity was used.

A mixture of the starting components was loaded into the 10–15 cm long quartz ampoules with a diameter of 1.5 cm. Moreover, the sequence of loading prevented the interaction between cadmium and mercury. Since manganese turns out to be active with respect to quartz, the ampoules were covered with graphite.

In all the cases doping impurity concentration N_V equaled to $1 \cdot 10^{19}$ cm^{-3}. Synthesis and growth temperatures were chosen experimentally since the state diagrams of the given solid solutions are unknown.

In course of synthesis the main attention was paid to the temperature ranges of the intensive reaction, i.e. (723–773 K) and (1110–1150 K), respectively. The rate of temperature increase didn't exceed 1 K/min.

The 2 mm thick wafers mechanically cut from the different parts of the single crystals were polished, lapped and then thoroughly cleaned with deionized water and toluene. In order to measure the values of dark R_d and light R_l resistance of the obtained crystals, gold from the solution of AuCl$_3$ was chemically deposited on the wafers and copper wires were soldered by means of indium. For the crystals under investigations the magnitude of R_d was found to lie within the $5 \cdot 10^6$–$5 \cdot 10^9$ Ω interval, while the R_d/R_l ratio ranged from 50 to 10^3.

Carrier concentration evaluated from the Hall effect measurements averaged to 10^8–10^{10} cm^{-3}, and obtained mobility values were of about 10^2–10^3 cm^2/V·sec.

Optical studies were carried out at 300 K on monochromator MDR-23 and IR spectrometer IRS-21.

Fig. 1 shows optical transmission spectra of the 1.5 mm thick wafers of Cd$_{1-x-y}$Mn$_y$Hg$_x$Te with $x = 0.05$; $y = 0.03$, $N_V = 1 \cdot 10^{19}$ cm^{-3} prepared from the different parts of the crystalline ingot. It's seen from the figure, that achieved transmission is up to 40 %. Moreover, the short-wave edge for the sample cut from the lower part of the crystal, which refers to beginning of solidification (curve A), and for the one prepared from the middle part of the ingot (curve B) almost overlap, being indicative of the crystalline homogeneity. Moving up the crystal towards its end, deterioration of the optical quality occurs (the value of transmission decreases to 26 %) and the short-wave edge is shifted to the range of lower energies (curve C). The latter fact evidentially points out some segregation of the components and existence of non-controlled residual impurities, which worsen the transmission.

For the wafers of Cd$_{1-x-y}$Mn$_y$Hg$_x$Te:V ($x = 0.05$; $y = 0.05, 0.07$, $N_V = 1 \cdot 10^{19}$ cm^{-3}), manufactured from the different parts of the crystalline ingot, transmission spectra measured in the 2–15 µm spectral range, reveal a distinguishable feature within 3.5–5.5 µm (Fig. 2). In particular, the transmission coefficient decreases rapidly down to its minimum, the depth of which differs for each wafer.

To clear up the nature of the absorption band let's examine the energy band diagram of vanadium levels in CdTe shown in Fig. 3 [13]. As one may notice, the crystalline field splits vanadium into the lower level of $^4T_1$(F) and two levels of $^4A_2$(F) and $^4T_1$(P) positioned higher by energy. The $^4T_1$(P) level is resonant, i.e. situated on the background of the continuos spectrum of the conduction band (CB).

Transition between $^4T_1$(F) and $^4A_2$(F) levels is intracentral and its energy equals 0.83 eV. The energy of 1.16–1.23 eV corresponds to the $^4T_1$(F)–$^4T_1$(P) intracentral transitions of elector with following autoionization of the one to conduction band. Direct photoionization of the V^{2+} centres $^4T_1$(F)–CB takes place at the energy of 1.05 eV.
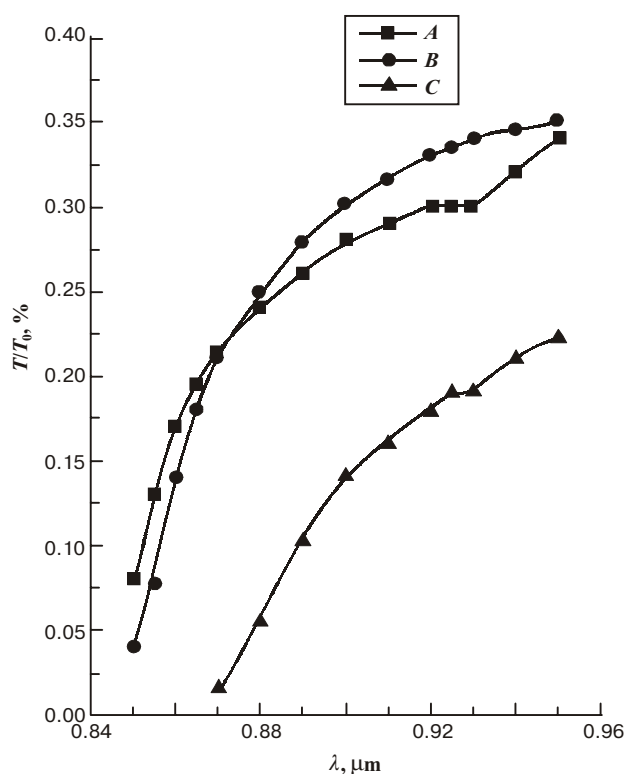

Fig. 1. Spectral dependence of the transmission coefficient of Cd$_{1-x-y}$Hg$_x$Mn$_y$Te:V ($x = 0.05$; $y = 0.03$), $N_V = 1 \cdot 10^{19}$ cm^{-3} (A – the beginning of crystallization, B – the middle part, C – the end of the crystal).
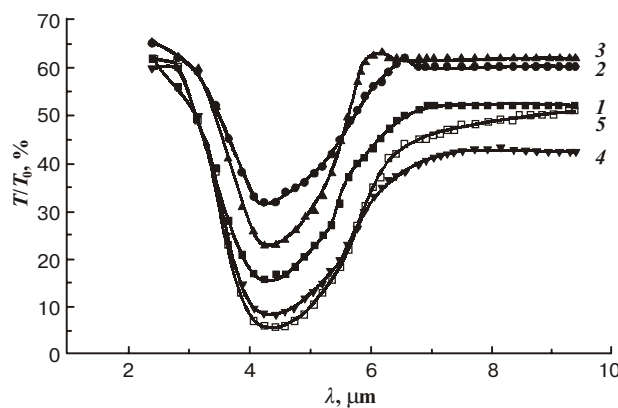

Fig. 2. Spectral dependence of the transmission coefficient of Cd$_{1-x-y}$Hg$_x$Mn$_y$Te:V ($x = 0.05$), $N_V = 1 \cdot 10^{19}$ cm^{-3} (1, 4, 5 – $y = 0.07$; 2, 3 – $y = 0.05$).

Thus, the named transitions can't bring about the absorption band with its maximum at 0.25–0.27 eV.

On the other hand, similar behavior of optical transmission spectra was observed for the CdTe crystals, doped with the Fe, Co and Cr impurities [14], which tend to form shallow donor levels under the bottom of conduction band. Analogously the revealed absorption band with its maximum in the named energy range can be assigned to manganese ions existing both in the Mn^{2+} and Mn^{1+} charge states. The Mn^{2+} state can't be identified with the transition observed in the experiment, since for the II-VI

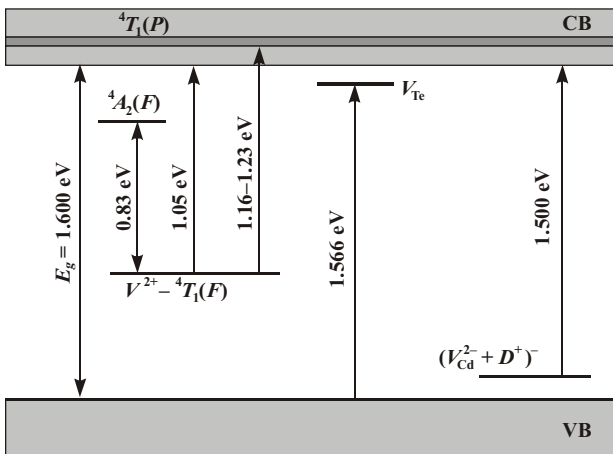**Fig. 3.** Energy level diagram and possible kinds of transitions in CdTe:V [13].

Fig. 4. Absorption coefficient spectra in Cd$_{1-x-y}$Hg$_x$Mn$_y$Te:V taken at 300 K, $N_V = 1 \cdot 10^{19}$ cm^{-3}.

semiconductor it is situated deep in the valence band. However, according to [15], on the basis of theoretical calculations manganese has been proved to exist in the Mn^{1+} charge state in the CdTe:V:Mn crystals. It has been shown, that co-doping of cadmium telluride with the mentioned impurities results in significant enhancement of photorefractive two-wave mixing gain due to presence of the additional donor ionization level in band gap, introduced by the Mn^{1+} centers. Energy position of this level found theoretically amounts to $E_{VB} + 1.4$ eV [15]. Thus, experimentally revealed minimum of optical transmission can be attributed to the photoionization transition Mn$^{1+} + h\nu \rightarrow$ Mn$^{2+} + e$.

The influence of manganese on the absorption spectra is demonstrated in Fig. 4, where the dependence of the absorption coefficients on photon energy is shown. The band gap E_g of the solid solutions of Cd$_{1-x-y}$Mn$_y$Hg$_x$Te:V ($x = 0.05$) for the compositions of $y = 0.03, 0.05, 0.07$ equals 1.44, 1.45 and 1.48 eV, respectively. I.e. the increases of manganese content, with the mercury mole fraction being constant, causes the shift of the absorption edge to high-energy region. It should be noted, that optical absorption coefficient for each manganese content was investigated on the samples with a thickness ranging from 0.25 to 1.1 mm. A magnitude of E_g was determined by extrapolation of $\alpha^2 = f(h\nu)$ to the intersection with the photon energy axis (see Fig. 4).

An attempt to correlate the experimental values of the band gap with those found according to the $E_g(x, y)$ expressions presented in [1, 2, 4, 9] didn't yield any positive results. It's more likely to be connected with the fact, that the given relationships are valid only for compositions with the small cadmium content.

The values of E_g calculated according to the following expression given in [6] showed the best agreement with the experimental findings: $E_g = 1.46z - 1.62x + 1.33y$. In the case of $x = 0.05$; $y = 0.03$; $z = 0.92$ ($1 - x - y = z$) calculated value of E_g equals to 1.3 eV, while for $x = 0.05$; $y = 0.07$; $z = 0.88–1.29$ eV.

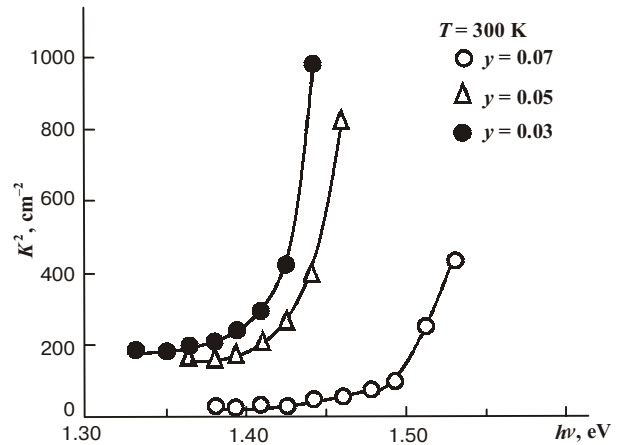Thus, it follows from the investigations carried out, that semi-insulating state with high photosensitivity are

accomplished in the quaternary solid solutions. The optical transmission spectra of Cd$_{1-x-y}$Mn$_y$Hg$_x$Te:V ($x = 0.05$), $N_V = 1 \cdot 10^{19}$ cm^{-3} with manganese content $y = 0.05; 0.07$ exhibit a minimum, resulting from the photoionization transition Mn$^{1+} + h\nu \rightarrow$ Mn$^{2+} + e$. The band gap width of the given quaternary solid solutions determined from optical investigations appears to grow with increase of manganese concentration and at $x = 0.05$ for the corresponding compositions of $y = 0.03, 0.05$ and 0.07 E_g equals 1.44, 1.45 and 1.48 eV. Disagreement between these values and those calculated for each manganese content points out a need for foundation of new theoretical patterns enabling to establish parameters and characteristics of such wide-gap semiconductors.

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