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Self-purification effect in CdTe:Gd crystals

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Abstract. The temperature dependences (T = 80 – 420 K) of the concentration of charge carriers and the Hall mobility in undoped CdTe and CdTe:Gd single crystals grown by the Bridgman method are studied. It is found that the conductivity type of CdTe:Gd crystals changes with increase in the impurity concentration in the melt: n-conductivity at 5.10^{17} – 3.10^{18} cm^{-3} and p-conductivity at 3.10^{18} – 10^{19} cm^{-3}. The concentrations and ionization energies of A_1 (E_{A1} = 0.05 eV) and A_2 (E_{A2} = 0.12-0.15 eV) acceptors are determined from the temperature dependences of the Hall coefficient and the mobility of carriers. A long-term thermal treatment of gadolinium-doped p-CdTe crystals in the range 663 – 713 K is accompanied by the "self-purification" of the material from A_2-acceptors and compensating donors. The Gd impurity at $C_0 > 3.10^{18}$ cm^{-3} is shown to bring no new electrical active centers into the CdTe lattice, by reducing, at the same time, the background of residual impurities. It is suggested that Te precipitates and Te inclusions serve as sinks for the above defects.

Keywords: semiconductors, cadmium telluride, doping, electron conduction, Hall effect.

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1. Introduction

Cadmium telluride has been intensively studied lately as a promising material for numerous applications including photonics [1]. Optical and magnetooptical studies of CdTe doped with Gd reveal several characteristic properties of the material such as a large enhancement of the Faraday rotation [2, 3]. To be integrable in industrial components, semiconductors need to contain charged scattering centers in low concentrations. The doping of semiconductor crystals, in particular of semiconductors of the III-V and IV-VI groups, with rare-earth elements is accompanied by their purification from uncontrolled impurities (it is the so-called "self-purification" effect) [4]. A similar effect is observed in doped cadmium telluride crystals and has practically not been studied yet. This paper presents the electrophysical characterization of CdTe crystals doped with gadolinium. The effect taking place when the doping level of CdTe is greater than $3{\cdot}10^{18}$ cm^{-3} is discussed.

2. Experimental procedure

Undoped CdTe and CdTe:Gd single crystals were grown by using the Bridgman method under the same technological conditions. The doping of cadmium telluride single crystals with the Gd impurity was carried out according to the Cd-Te-Gd pattern without excess tellurium. To avoid the reaction of Gd with quartz even protected with a pyrolytic graphite layer at high temperatures, the doping was made during the synthesis. The master alloy concentration in the melt (C_0) varied from $3{\cdot}10^{17}$ to $3{\cdot}10^{19}$cm^{-3}. The doped crystals have the n-type conductivity at $C_0 < 3{\cdot}10^{18}$ cm^{-3} and the p-type one at $C_0 > 3{\cdot}10^{18}$ cm^{-3}. Exactly the p-CdTe-Gd crystals will be discussed in the present paper. The Gd-doped p-CdTe crystals were heated (during 24 – 120 h) in evacuated quartz ampoules.

The temperature dependences (T = 80 – 400 K) of the concentration of holes (p) and their Hall mobility (μ_p) were studied by measuring the Hall coefficient and the electrical conductivity of samples as functions of the

Table. Long-term thermal treatment (LTT) of CdTe-Gd crystals.

Sample	C_0, cm^{-3}	g	LTT conditions		Parameters after LTT			
			T, K	τ, h	E_{A2}, eV	μ_{80}/μ_{300}	$[A_2]\cdot10^{-15}$, cm^{-3}	$[A_1]\cdot10^{-16}$, cm^{-3}
1	$3\cdot10^{18}$	0.33	723	48	0.114	8.4	7.3	3.6
2	$3\cdot10^{18}$	0.47	693	100	0.135	14.5	7.7	0.3
3	$3\cdot10^{18}$	0.47	713	72	0.120	11.0	7.3	1.6
4	$3\cdot10^{18}$	0.47	753	24	0.040	7.3	–	19.0
5	$3\cdot10^{18}$	0.68	673	100	0.139	13.4	12.0	0.7
6	$3\cdot10^{18}$	0.68	693	90	0.137	13.0	11.0	1.0
7	$3\cdot10^{18}$	0.68	753	24	0.043	5.7	–	33.0
8	10^{19}	0.38	673	90	0.150	10.5	7.0	1.3
9	10^{19}	0.86	673	90	0.144	10.0	21.0	1.6
10	$3\cdot10^{19}$	0.72	673	120	0.152	11.1	15.0	1.6

Note. μ_{80}/μ_{300} is the ratio between 80 K and room temperature Hall mobilities.

reduced axial coordinate (g) in doped ingots: $g = \chi/L$, where χ is the coordinate counted from the beginning of the crystal, and L is the ingot length.

3. Results and discussion

It was found that, in p-CdTe-Gd samples and in CdTe, the conductivity is controlled only by one acceptor A_2 (ionization energy E_{A2} = 0.12-0.15 eV [5]). The ionization energy E_{A2} is a function of χ at $C_0 = 3\cdot10^{18}$ cm^{-3} and remains constant at the heavier doping of the melt (Fig. 1). Assuming that, in the crystals under study, there is a modification of A_2-acceptors by the presence of Gd impurity, as was earlier demonstrated for CdTe-Yb crystals [6], the following suggestions can be made. First, the coefficient κ of the Gd segregation in CdTe is essentially less than unity and, second, the solubility of the impurity is so low that, at $C_0 = 3\cdot10^{18}$ cm^{-3}, the quantuty $k\cdot C_0$ is limited by the boundary solubility. The low content of the Gd impurity in the main crystal part (g = 0–0.95) is indicated by the results of magnetic investigations [3]. Even in the heaviest doped samples at 100 K, the paramagnetic component of the magnetic susceptibility does not exceed $0.03\cdot10^{-6}$ cm^3/g, which gives the value of 10^{18} cm^{-3} for the Gd concentration in the grown crystals. Thus, practically the entire master alloy is pressed back to the end of ingots (g > 0.95), where strong paramagnetism is really observed.

The concentrations of A_2-acceptors and fully compensated A_1-acceptors as functions of the reduced axial coordinate g are shown in Figs. 2 and 3. It is seen that, at g < 0.4, the concentration of A_2-acceptors ($[A_2] = (5–7)\cdot10^{15}$ cm^{-3}) is close to that in the undoped crystals. But, at g > 0.4, it increases abnormally fast, by showing the tendency to saturate at g > 0.8. The dependence of $[A_2]$ on C_0 at g < 0.4, as well as the nonmonotonous character of this dependence for g > 0.5 for alloys of different purities, testify that the donor component of the A_2 complex is due to noncontrolled impurities both in the source components and in Gd.

For low g values, no effect of the impurity on $[A_1]$ can be spotted (Fig. 1). But, at g > 0.4, a "purification" of the crystal matrix from A_1-acceptors due to the introduction of the Gd impurity occurs. As will be shown below, this effect is not directly related to the pressing of A_1-acceptors back to the end of the ingot due to the segregation on the crystallization front, but it is caused by the transition of A_1-acceptors to an electrically inactive state (precipitation, trapping by other phase inclusions, in particular, by tellurium, etc. [7]). We suggest that the Gd impurity intensifies the processes leading to the formation of tellurium-enriched precipitates and inclusions which serve as sinks for A_1-acceptors. The possibility of such an intensification is caused by the existence of a series of chemical compounds ($GdTe_2$, $GdTe_3$), as well as their eutectics with tellurium in the Gd-Te system. The total concentration of A_1-acceptors increases with g. However, the concentration of sinks increases also, so the $[A_1](g)$ dependence has a nonmonotonous character. The optimal ratio between the concentrations of the former and the latter is provided at minimum $[A_1]$ values (g = 0.5–0.7). If this suggestion is correct, then the thermal treatment of Gd-doped samples depending on the thermal treatment conditions must be accompanied both by a further "purification" of the material from A_1-acceptors and by its "contamination". The effect of a long-term thermal treatment on the parameters of CdTe-Gd crystals is given in Table.

The first evident conclusion following from the above-presented data is that the upper bound of the self-purification temperature range is lowered as compared with that of undoped crystals. In particular, the long-term thermal treatment at 753 K is accompanied by the full decompensation of A_2-acceptors due to a drastic increase in the concentration of A_1-acceptors, which controls the p-conduction at low temperatures. It turned out that the higher the values of g and the Gd impurity concentration in the melt, the stronger the "contamination" of samples with A_1-acceptors. After the long-term thermal treatment at 723 K, the contamination of

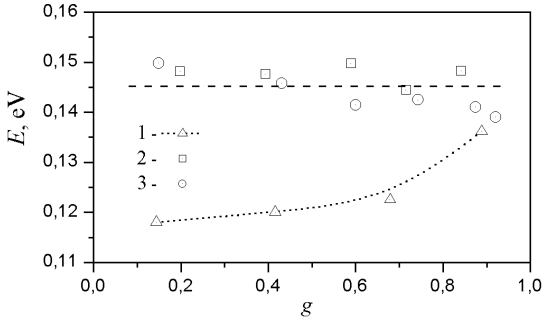

Fig. 1. Axial distribution of the ionization energy of A_2-acceptors in *p*-CdTe-Gd crystals for different C_0 values: *1* – $3\cdot10^{18}$; *2* – 10^{19}; *3* – $3\cdot10^{19}$ cm^{-3}.

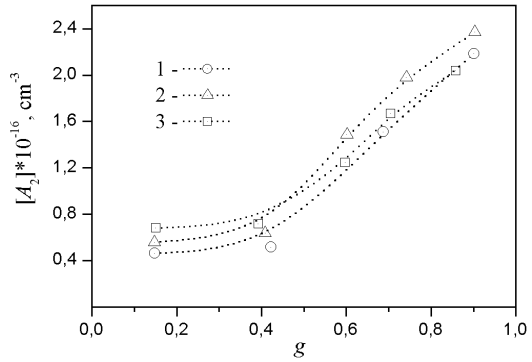

Fig. 2. Axial distribution of the concentration of A_2-acceptors in *p*-CdTe-Gd crystals for different C_0 values: *1* – $3\cdot10^{18}$; *2* – 10^{19}; *3* – $3\cdot10^{19}$ cm^{-3}.

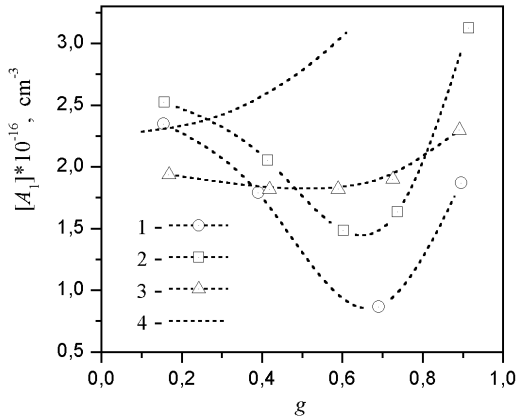

Fig. 3. Axial distribution of the concentration of A_1-acceptors in *p*-CdTe-Gd crystals for different C_0 values: *1* – $3\cdot10^{18}$; *2* – 10^{19}; *3* – $3\cdot10^{19}$ cm^{-3} ; *4* – undoped CdTe.

samples with A_1-acceptors is less noticeable, and A_2-acceptors continue to control the conductivity. Hence, it can be asserted that the upper temperature bound of the effective "self-purification" of Gd-doped samples does not exceed 713 K.

The lowest concentrations of A_1-acceptors were obtained after the long-term thermal treatment at 673–693 K on samples containing the smallest amounts of Gd. The temperature area of the effective "self-purification" was then shifted even lower, but the samples required a very long thermal treatment. We note that the "self-purification" effect during a long-term thermal treatment is always accompanied by an increase in the ionization energy of A_2-acceptors, which testifies that the "purification" from compensating donors occurs simultaneously. No unambiguous conclusions can be made as for the "self-purification" from A_2-acceptors, since changes in $[A_2]$ under a long-term thermal treatment are relatively small.

4. Conclusion

A long-term thermal treatment (τ = 100 h) of Gd-doped *p*-CdTe crystals in the temperature region of 663–713 K is accompanied by the "self-purification" of the material from A_2-acceptors and compensating donors. Precipitates and inclusions containing tellurium serve as sinks for the polluting species. The temperature decrease in the area of the effective "self-purification" is caused by the enrichment of sinks with gadolinium forming compounds with Te. In particular, the eutectic temperature of $GdTe_3$+Te equal to 673 K gets just into the "self-purification" area.

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