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Water — a source electrically active centres in CdHgTe

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Influence of water solutions with various pH and electrochemical treatment in cathode position on concentration of charge carriers in samples $Cd_xHg_{1-x}Te$ with $x = 0.2{-}0.3$ is investigated. Cathodic treatment cadmium-mercury-tellurium at small density current increases concentration of donors, and at high density acceptors are formed. It is supposed that hydroxyl groups create acceptors centers, introduce in interstitial cadmium-mercury-tellurium. At treatment for a long time (it is more than 20 h) or acceptors are formed with concentration at level of $10^{16}\,\mathrm{cm}^{-3}$ (at high activity of hydrogen), or donors with concentration of $10^{14}\,\mathrm{cm}^{-3}$ (at low activity of hydrogen) are uniform distribution on all thickness of cadmium-mercurytellurium film and does not vary with the subsequent increase in time of treatment.

Keywords: CdHgTe, electrochemical treatment, acceptors, activity of hydrogen.

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1. Introduction

It has been demonstrated in several studies [1–3] that electrically active centers are produced in cadmium mercury telluride $Cd_xHg_{1-x}Te$ (CMT) processed in aqueous media. Specifically, acceptors with concentrations up to $10^{19}\,\mathrm{cm}^{-3}$ are produced in CMT films boiled in deionized water [1]. Layer-by-layer etching reveals a diffusion distribution of acceptors over the CMT film thickness in this case, and no foreign electrically active impurities are identified by mass spectrometry. The nature of forming acceptors remains obscure, and it is not known whether the presence of water is a sufficient condition for acceptor production in CMT. Relying on the data from [4], where the transfer of deuterium from heavy water to CMT and the formation of acceptors during boiling were reported, and [5], where calculations were preformed to demonstrate that hydrogen may act as an amphoteric impurity in CdTe, the authors of [2] have hypothesized that the introduction of acceptors into CMT under boiling may be attributed to the implantation of hydrogen into CMT. The model of acceptor formation due to hydrogen in the course of water dissociation raises doubts in relation to the fact that the oxygen–hydrogen binding energy is high.

Since processing in aqueous solutions is a common stage of the technological procedure of fabrication of CMT devices, it is of interest to clarify the nature of electrically active centers produced by water in CMT.

2. Experimental results and discussion

The effect of boiling in aqueous solutions with various pH values and electrochemical treatment in the cathode position (cathode treatment, CT) on the Hall parameters of charge carriers in CMT samples was examined. Heteroepitaxial $Hg_{1-x}Cd_xTe/CdTe/ZnTe/Si(013)$ structures with variband layers grown by molecular-beam epitaxy (MBE) were used [6]. The CdTe content was $x = 0.22$ and $x = 0.30$ in the absorbing CMT layer and reached $x = 0.45$ in the upper variband layer. The compositional distribution over the thickness of CMT layers was determined in the process of growth with a built-in single-wave ellipsometer (Fig. 1).

Boiling in deionized water with small added amounts of hydrochloric acid or ammonia was performed in a quartz vessel. Water was purified and deionized using a SUPER-Q PLUS (Millipore) system. The resistance of water at the outlet of this system was close to 18 MΩ/cm. The results of layer-by-layer measurements of samples boiled in deionized water revealed that the concentration of holes at

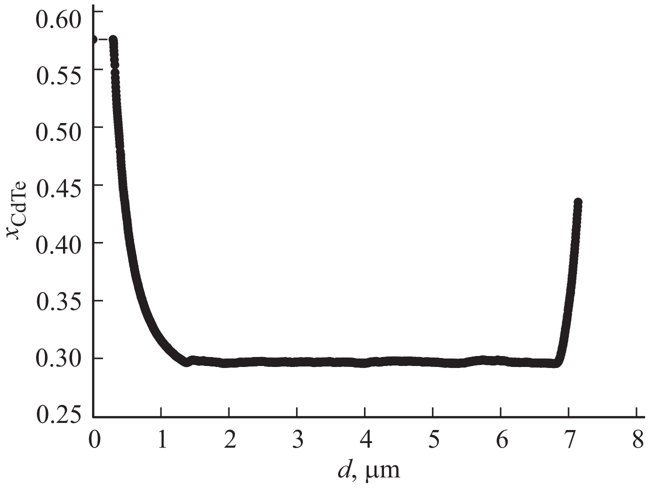

Figure 1. Compositional distribution over the thickness of CMT layers measured in the process of growth with an automatic ellipsometer. Thickness values are measured from the interface with a buffer CdTe layer.

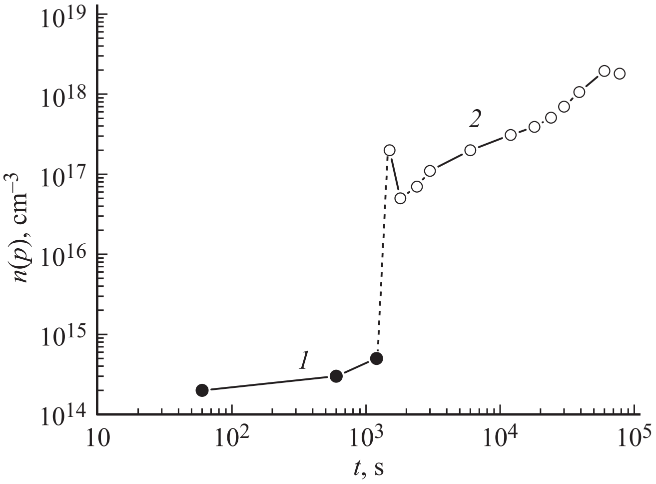

Figure 2. Experimental dependence of the effective concentration of carriers (electrons — *1*; holes — *2*) on time of boiling in deionized water. Measurements were performed in magnetic fields $B = 0.05\,\mathrm{T}$ and $B = 1.0\,\mathrm{T}$ for *n*-type and *p*-type carriers, respectively.

the surface increases in the process of boiling and reaches a value of $10^{19}\,\mathrm{cm}^{-3}$, while the concentration in the bulk of a film drops sharply. This dependence of the carrier concentration at the surface on processing time indicates that an equilibrium acceptor concentration in the near-surface layer is not reached and the production of acceptors is limited by kinetic processes. The hole concentration did not reach saturation in the course of boiling.

Hall measurements of films nonuniform over their thickness allow one to characterize the process of introduction of acceptors. If different types of charge carriers with comparable contributions to the measured electrophysical parameters are present, Hall measurements in a constant magnetic field yield effective values. Figure 2 presents the variation of effective concentration of electrons (holes) $n(p) = 1/(qR_H)$ with time of boiling in deionized water.

All CMT samples with electronic conductivity change their conductivity type in the process of boiling. The conductivity type and the effective concentration change abruptly on reaching a certain boiling time. The time needed to change the conductivity type varies slightly even from one region of a heteroepitaxial plate to the other. This is likely to be an indication of the fact that a certain kinetic barrier, which depends on the surface state, needs to be overcome to produce acceptors.

Being a weak electrolyte, water dissociates into ions:

$$\mathrm{H_2O}_l = \mathrm{H}_s^+ + \mathrm{OH}_s^-. \tag{1}$$

Hydrogen ions are present in water in the form of hydroxonium $\mathrm{H_3O^+}$ ions, but water associated with a hydrogen ion is omitted in (1) for simplicity.

The equilibrium constant of reaction (1) is written as

$$\mathrm{K} = x_{\mathrm{H}^+} \cdot x_{\mathrm{OH}^-} / x_{\mathrm{H_2O}},$$

where $x_{\mathrm{H_2O}}$, x_{H^+}, and x_{OH^-} are the molar fractions of water, hydroxonium ions, and hydroxyl ions, respectively.

The state of equilibrium in a dissociation reaction in homogeneous systems is characterized by dissociation degree α, which is equal to the ratio of number n of dissociated molecules of a substance to overall number N of its molecules:

$$\alpha = n/N.$$

The results of measurements of the electrical conductivity of pure water demonstrated that water at 100°C has dissociation degree $\alpha_{373\,\mathrm{K}} = 1.3 \cdot 10^{-8}$ [7]. Since the dissociation degree is low and, consequently, the molar fraction of water is equal to unity, the molar fraction of ions in the solution is almost equal to the dissociation degree squared:

$$K_{373\,\mathrm{K}} = \alpha^2 = 1.69 \cdot 10^{-16}.$$

The molar fractions of hydroxonium and hydroxyl ions are interrelated via the equilibrium constant of reaction (1): an increase in the molar fraction of one type of ions leads to a reduction in the molar fraction of ions of the other type. The concentrations of hydrogen ions and hydroxyl ions in pure water are equal. The ratio between the numbers of hydroxonium and hydroxyl ions shifts after the introduction of acids or alkalies into water. The dissociation degree of hydrochloric acid and ammonia in dilute solutions is close to unity. Therefore, $x_{\mathrm{H}^+} = 0.01$ and $x_{\mathrm{OH}^-} = 0.005$ correspond to the used 0.01 N solution of hydrochloric acid and 0.005 N solution of ammonia, respectively. The acidity of an aqueous medium exerts a strong influence on the number of acceptors introduced in the process of boiling (see Table 1).

It follows from Table 1 that the number of introduced acceptors decreases as the concentration of hydroxonium ions increases; at the same time, the molar fraction of hydroxyl groups in an aqueous solution and the concentration of introduced acceptors are correlated. Acceptors with a concentration $> 10^{16}\,\mathrm{cm}^{-3}$ averaged over the film thickness are introduced after 45 min of boiling in deionized (DI) water and a dilute ammonia solution. In contrast, longer-term boiling (90 min) in a dilute solution of hydrochloric acid does not alter the conductivity type, suggesting that the number of introduced acceptors is insignificant. This result contradicts the hypothesis that acceptors are produced by hydrogen atoms in CMT in the process of boiling.

Equilibrium is not established in the considered examples of experiments on boiling. This is evidenced by the results of layer-by-layer Hall measurements in boiled samples (the concentration of acceptors in their near-surface layer increases with time of boiling) and the non-reproducibility of the time to an electron–hole conductivity transition in the process of boiling. This suggest that an activation barrier needs to be overcome to incorporate acceptors into CMT and that there is not enough time for diffusion equalization over the CMT film thickness. However, it is evident that the acceptor concentration depends on molar fraction x_{H^-}

Table 1. Electrical parameters of charge carriers in MBE CMT samples after boiling in media with different acidity levels

Treatment	Thickness, μm	Effective concentration, cm^{-3}	Effective mobility, cm^2/(V^{-1} · c^{-1})	Conductivity, $\Omega^{-1} \cdot$ cm^{-1}	x_{H^+}	x_{OH^-}
Non-processed initial	9.1	$n = 5.5 \cdot 10^{14}$	$7.2 \cdot 10^4$	6.84		
Boiling, 0.01 N HCl, 90 min	9.1	$n = 2.7 \cdot 10^{14}$	$6.7 \cdot 10^4$	3.02	$1 \cdot 10^{-2}$	$1.7 \cdot 10^{-14}$
Boiling, DI H_2O, 45 min	9.1	$p = 1.2 \cdot 10^{16}$	330	0.65	$1.3 \cdot 10^{-8}$	$1.3 \cdot 10^{-8}$
Boiling, 0.005 N NH_4OH, 45 min	9.1	$p = 1.4 \cdot 10^{16}$	340	0.78	$3.4 \cdot 10^{-14}$	$5.0 \cdot 10^{-3}$

Table 2. Concentration and mobility of carriers in MBE CMT samples with $x = 0.221$ processed under different pressures of components

Sample number	Treatment	Effective concentration, cm^{-3}	Effective mobility, cm^2/(V^{-1} · c^{-1})	Conductivity, Om^{-1} · cm^{-1}	P_{Hg}, Torr
	Initial	$n = 4.9 \cdot 10^{14}$	$4.2 \cdot 10^4$	3.50	
1	Boiling for 1 h in a 0.005 N solution of ammonia	$p = 4.7 \cdot 10^{16}$	245	1.85	
1-1	Annealing for vacancy filling at 226°C (220°C Hg), 20 h	$p = 7.4 \cdot 10^{16}$	430	5.11	10^1
1-2	Annealing at 200°C, 24 h (no mercury, tellurium activity is close to unity)	$p = 7.9 \cdot 10^{16}$	314	4.01	10^{-2}
1-2	Annealing for vacancy filling at 226°C (220°C Hg), 20 h	$p = 7.5 \cdot 10^{16}$	297	3.58	10^1

of hydroxyl ions in a solution: the higher x_{H^-} is, the greater is the number of acceptors introduced into CMT.

The possible relation between acceptors produced in boiling and the activity of CMT components was probed. The concentrations of point defects associated with CMT components should vary with vapor pressure of components in the environment if the conditions are suitable to reach near-equilibrium. The CMT homogeneity range allows one to vary the vapor pressure of mercury and tellurium within several orders of magnitude without damage to CMT. If acceptors produced during boiling occupy CMT lattice sites, such processing should alter the acceptor concentrations by several orders of magnitude. If acceptors occupy metal sublattice sites, their concentration is expected to decrease as a result of annealing in saturated mercury vapor. If, however, acceptors occupy tellurium sublattice sites, their concentration should decrease in the course of annealing under a minimum mercury pressure (and, consequently, a maximum tellurium pressure). Samples with acceptors introduced during boiling were processed under marginal conditions: at a tellurium activity of unity and at a mercury activity of unity. Just as in the earlier studies [1], it was found that acceptor centers do not get annihilated after annealing in saturated mercury vapor under such conditions in which point defects in thin CMT films get close to equilibrium with the environment (temperature: > 200°C; duration: more than 20 h). This implies that centers are not associated with metal sublattice sites in CMT. The results of processing are listed in Table 2.

Sample 1 boiled in a 0.005 ammonia solution was processed. This sample became *p*-type following boiling. After that, sample 1 was cut into two parts: 1-1 and 1-2. Sample 1-1 was annealed under a maximum mercury vapor pressure. Just as in the earlier study [1], it was found that acceptor centers do not get annihilated after annealing in saturated mercury vapor under such conditions in which point defects in thin CMT films get close to equilibrium with the environment (temperature: > 200°C; duration: more than 20 h). Thus, one may conclude that centers are not associated with vacancies in the metal sublattice. The enhancement of acceptor concentration in sample 1-2 after annealing under a minimum mercury pressure was the same as the one achieved in sample 1-1 annealed under a maximum mercury pressure; i.e., acceptors did not

Table 3. Influence of the regimes of electrochemical treatment on the electrical parameters of samples

	Initial after growth	Sample 1, CT 72 h, 2 μA/cm^2	Sample 2, KO 24 h, 24 μA/cm^2	Sample 3, CT 74 h, 20 μA/cm^2	Sample 4, CT 100 h, 68 μA/cm^2
Carrier concentration, cm^{-3}	$n = 4.9 \cdot 10^{14}$	$n = 6.1 \cdot 10^{14}$	$n = 8.3 \cdot 10^{14}$	$p = 4.6 \cdot 10^{16}$	$p = 5.1 \cdot 10^{16}$
Mobility, cm^2/(V$^{-1} \cdot$ c^{-1})	$4.2 \cdot 10^4$	$5.0 \cdot 10^4$	$9.7 \cdot 10^3$	232	345
Conductivity, $\Omega^{-1} \cdot$ cm^{-1}	3.50	5.59	1.30	1.72	2.86

Note. CT stands for cathode treatment.

occupy mercury sites in sample 1-1 and tellurium sites in sample 1-2. The acceptor concentration enhancement is greater than the concentration of vacancies ($\sim 10^{16}$ cm^{-3}) that were supposed to be produced under the considered annealing conditions. One is tempted to suggest that not all of the hydroxyl groups at the surface, which were produced during boiling, detach and move into the bulk of a CMT film in the process of boiling and that higher-temperature heating enhances the conductivity compared to boiling. Annealing of sample 1-2 for vacancy filling under a saturation mercury vapor pressure resulted in a $\sim 10\%$ conductivity reduction, which corresponds to the contribution of vacancies produced in the course of annealing under a minimum mercury vapor pressure. These data suggest that the activity of CMT components has no effect on the number of acceptors introduced during boiling and that hydroxyl groups have the capacity to produce acceptor centers by occupying interstitial sites in CMT.

The concentration of hydroxonium and hydroxyl ions near the CMT surface may be controlled by adjusting the solution acidity and via electrochemical treatment. The EMF of a normal oxygen–hydrogen cell is 1.23 V and varies slightly with concentration of ions. At electrode voltages lower than the normal potential, hydrogen reduction is not observed, and the voltage is compensated by polarization due to the formation of double electric charge layers at electrodes. The clustering of hydroxonium ions at the cathode leads to a reduction in the concentration of hydroxyl ions at the CMT surface, and the introduction of acceptors with these ions is suppressed.

The probability of acceptor production driven by hydroxyl ions decreases even more if the cathode overvoltage increases and hydrogen gets produced. The process of production of molecular hydrogen at the cathode is two-stage: first, a hydroxonium ion discharges as a result of an electrochemical process, and a hydrogen atom emerges on the cathode surface. Owing to repulsion of like-charged hydroxonium ions, hydrogen atoms do not form at nearby points on the cathode surface. Therefore, the purely chemical process of integration of hydrogen atoms into a molecule takes a certain time to complete. When atomic hydrogen is present on the surface, hydroxyl ions may be reduced to a water molecule and the acceptor concentration in CMT may decrease.

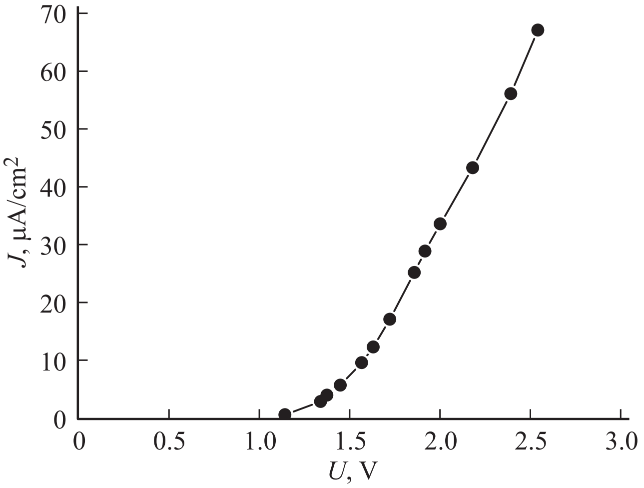

Figure 3. Current–voltage curve of the electrolytic cell. Anode — pyrolytic graphite; cathode — MBE CMT HES; electrolyte — 0.004 N solution of H_2SO_4.

CMT was subjected to electrochemical treatment in a 0.004 N solution of sulfuric acid. A pyrolytic graphite plate served as the anode, and a sample cut from an MBE CMT heteroepitaxial structure (HES) was the cathode. The current–voltage curve of the cell is shown in Fig. 3.

Table 3 illustrates the effect of different regimes of electrochemical treatment on the electrical parameters of samples prepared from the same structure.

Samples were cut from one and the same MBE CMT HES on a silicon substrate; the CMT film thickness was 7.8 μm, $x = 0.22$. Parameters were determined in Hall measurements at 77 K in a magnetic field of 0.05 T (n-type) and 1.0 T (p-type).

The conductivity of an n-type CMT film increased slightly as a result of CT with a low current density of $1-3\,\mu$A/cm^2 (sample 1) that did not lead to the release of elementary hydrogen. At a high current density of $20-30\,\mu$A/cm^2 (samples 2 and 3), hydrogen was released and acceptors were produced in a CMT film. This led to a reduction in the conductivity of n-type sample 2 at a CT duration of

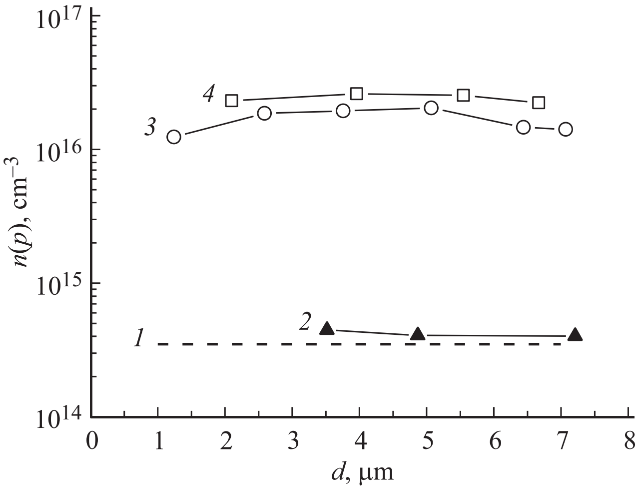

Figure 4. Results of layer-by-layer measurements of the carrier concentration over the thickness of samples subjected to CT: *1* — electron concentration in the initial sample; *2* — electron concentration after CT at $2\,\mu$A/cm^2, 72 h; *3, 4* — hole concentration after CT at $24\,\mu$A/cm^2, 100 h. Thickness values are measured from the interface with a buffer CdTe layer.

~ 20 h. If the cathode treatment continued for more than 40 h, samples became *p*-type (samples 3 and 4).

The carrier concentration in samples after CT was distributed uniformly over the entire CMT film thickness (Fig. 4). The acceptor concentration in *p*-type samples did not vary as the treatment time increased further. With the current density and the voltage raised to $60-70\,\mu$A/cm^2 and > 2.4 V, the acceptor concentration again did not increase in any significant manner; it just varied slightly from one sample to the other.

In contrast to acceptors produced in the process of boiling, which did not reach saturation concentration, acceptors produced during CT of a sufficient duration (more than 20 h at room temperature) reached a concentration of $10^{16}\,\text{cm}^{-3}$ and were distributed uniformly over the entire CMT film thickness ($\sim 10\,\mu$m). The indicated concentration remained unchanged in further treatment. The electrophysical parameters of samples switching to *p*-type conductivity in the process of cathode treatment remained unchanged during storage at room temperature in air; i.e., acceptors produced in CMT by hydrogen are resistant to oxidation. The acceptor concentration in such samples increased during heating both in air and in an inert atmosphere.

According to experimental data, hydrogen atoms produced on the CMT surface in the course of electrolysis of water induce the formation of acceptors in CMT if the activity level is sufficient. The concentration of forming electrically active centers is independent of the current density and the treatment duration and depends on the sample used. This behavior corresponds to a model where hydrogen atoms are not electrically active in CMT or have a low concentration ($< 10^{14}\,\text{cm}^{-3}$). At the same time, they may produce acceptors with concentrations in excess of $10^{16}\,\text{cm}^{-3}$ if the activity of hydrogen in interaction with neutral centers present in CMT is sufficiently high.

3. Conclusion

Water may act as a source of acceptor centers in CMT. The number of produced acceptor centers increases with concentration of hydroxyl groups in a solution, temperature, treatment time, and amount of water available and may reach $10^{19}\,\text{cm}^{-3}$. No effect of the activity of CMT components on the number of electrically active centers produced during boiling was observed. These factors combined suggest that hydroxyl groups have the capacity to produce acceptor centers by occupying interstitial sites in CMT. The obtained results indicate that the temperature and the time of contact with aqueous media should be minimized in technological procedures of fabrication of CMT-based photodetectors in order to suppress the formation of acceptor centers.

Hydrogen atoms formed in the course of water dissociation during CMT treatment in the cathode position may induce the emergence of acceptor centers in CMT if the current density is sufficiently high ($> 20\,\mu$A/cm^2). The concentration of these centers is independent of the treatment duration and the current density and depends on the sample subjected to processing. This is feasible if electrically active centers are produced in the interaction of hydrogen atoms with neutral centers present in CMT.

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Conflict of interest

The authors declare that they have no conflict of interest.

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