



Reverse ultrasonic changes of electrical conductivity in CdTe:Cl crystals

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ABSTRACT

Acousto-stimulated changes of electrical conductivity in low ohmic resistance *n*-type CdTe:Cl monocrystals are reversible and can be seen only during the ultrasonic influence. For the first time the long-term relaxation processes of the conductivity $\sigma(t)$ at ultrasound-on as well as at ultrasound-off have been found out. The relaxation $\sigma(t)$ is not monotonous generally, but, at least, has two stages. Acousto-active metastable defects are responsible for “instant” jump-like changes of the temperature dependence of conductivity $\sigma(t)$. The acousto-stimulated diffusion processes where the defining role belongs to dislocations, are responsible for long-term relaxation the temperature dependence of conductivity $\sigma(t)$. The main rebuilding process at ultrasound-on consists of the transformation of the charged acceptor complex into a neutral one.

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1. Introduction

Cadmium telluride (CdTe) monocrystals are used for the production of uncooling detectors of X- and γ -radiation for radiation monitoring of environment. Crystals impured with chlorine are very interesting from the point of view of practical application. Such crystals can replace tellurium in lattice nodes or paired with tellurium and cadmium vacancies form metastable complexes [1,2].

To improve the structural quality of crystals A_2B_6 different physical treatment is used: γ -irradiation, thermal annealing, hydrogen processing, microwave irradiation [3], and ultrasound treatment [4–7]. Taking into account the high density of dislocations ($\rho_{dis} \sim 10^{10} \text{ m}^{-2}$) and high efficiency of acousto-dislocation interactions, ultrasound (US) is turned out to be the most simple action from the listed above external actions, and can lead to the transformation of impurity-defect complexes and corresponding residual changes in electrical parameters of semiconductor crystals A_2B_6 (CdS, ZnS, CdTe, ZnCdTe, CdHgTe) [4–8]. The basic model that explains these changes is the dislocation one. The distribution of intensive ultrasonic wave causes dislocation vibrations; and, at intensities $W_{US} \sim 10^4 \text{ Wt/m}^2$ and $\rho_{dis} \sim 10^{10} \text{ m}^{-2}$ acousto-stimulate (AS) restructuring of defects can be observed actually in the whole volume of the sample. It is considered that under the influence of ultrasound wave so called “capture” or “release” of electrically active point defects of dislocations occurs, that are something like “collector” for them [5]. It is necessary to note that, depending on the state of impurity-defect structure (IDS) and parameters of US, the experiment can realize both residual changes and temporary ones observed only during the US influence.

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The peculiarity of the studied low-ohm resistance samples CdTe:Cl with from the point of view of US influence is not only high ρ_{dis} , but diversity of defective complexes containing additive Cl. It is known that in crystals with high conductivity concentration of donor centers $\text{Cl}_{\text{Te}}^+ > V_{\text{Cd}}^-$. Thus, part of Cl atoms is located on acceptor $[(V_{\text{Cd}}^-\text{Cl}_{\text{Te}}^+)^-]$ and neutral $[(V_{\text{Cd}}^-\text{2Cl}_{\text{Te}}^+)^0]$, and $[(V_{\text{Cd}}^-\text{Cl}_{\text{Te}}^+)^0]$ complexes. One more part of Cl atoms is captured by the dangling bonds on the dislocations. Thus, in conditions of US influence such a complex IDS of crystal in the result of AS increase of the diffusion coefficient of individual point defects (possible increase of the diffusion coefficient nearly 10^3 times [6]) can become significantly labile even at low temperatures (<300 K), that is favorable for investigate of AS effects. This paper focuses on the dynamic AS changes in electro-physical (EPH) properties of samples CdTe:Cl, the mechanism of which remains insufficiently-explored. This dynamic US influence when there are some reversible changes in detected conductivity, allows to monitor systematically the transients and kinetics of relaxation. Especially clearly such opportunity is realized in the pulsed mode of US loadings [7].

2. The samples and experiment

In this paper, the US influence on EPH characteristics of bulk monocrystal sample (size $\sim 2 \times 3 \times 8$ mm³) CdTe:Cl has been investigated. Cadmium telluride crystals have been obtained by Bridgman vertical method at low vapor pressure of cadmium in the ampoule. The concentration of chlorine impurities in the melt was $N_{\text{Cl}}^0 \approx 10^{24}$ m⁻³. Formation of ohmic contacts was being carried out by the method of thermal vacuum indium deposition at a temperature of 175 °C. To determine the parameters of the EPH (concentration n and mobility μ of charge carriers) in the temperature range 77–300 K by the Hall method in the regime of constant electric and magnetic fields was used. To measure EPH parameters in conditions of US loading (acousto-Hall method) nitric cryostat equipped with acoustic elements was used. It allowed us to perform measurements consistently on one sample with different states of IDS both in initial, and in acoustic excited, respectively [8]. US loading at the sample by longitudinal acoustic waves (frequency ~ 10 MHz, the intensity of $\sim 10^4$ Wt/m²) was being carried out through a buffer dielectric plate from piezoelectric transducer – lithium niobate plates (Y+36°)-section to which a sinusoidal signal from HF generator was being applied (see Insert on Fig. 2). The accuracy of measurement of electrical signals $\sim 10^{-6}$ V, temperature ~ 0.1 K. The change of the sample's temperature while measuring in conditions of intensive US loading during the time of measurement of definite experimental point didn't exceed 2–3 K.

3. Result and discussion

It was determined that the observed AS changes of Hall coefficient R_H and conductivity σ are reversible. While turning on US and after finishing the acoustic influence, slow (50–500) sec, takes place, depending on the temperature of the sample and the US intensity setting of parameters of the sample and their return to their initial state, respectively. In Figs. 1–3 you can see already relaxed (established) parameters.

3.1. Temperature dependence of the electrical conductivity and carrier concentration

Fig. 1 shows the temperature dependence of the electrical conductivity $\sigma(T)$ and the electron concentration $n_e(T)$. Curve 1 corresponds to the initial characteristics of crystal – without US influence and curve 2 – with US loading.

As depletion of energy becomes apparent at low temperatures ($T \approx 77$ K), we can assume that the depth of the shallow donor level in the studied crystals of CdTe:Cl is <0.01 eV. According to the published data such energy level corresponds to

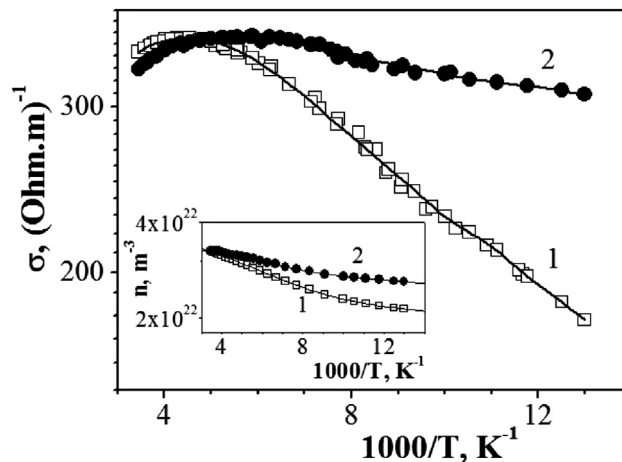


Fig. 1. CdTe:Cl. Temperature dependence of electrical conductivity and electron concentration (in insert): light point - without US; black point –US influence $W_{\text{US}} \approx 2 \cdot 10^4$ Wt/m².

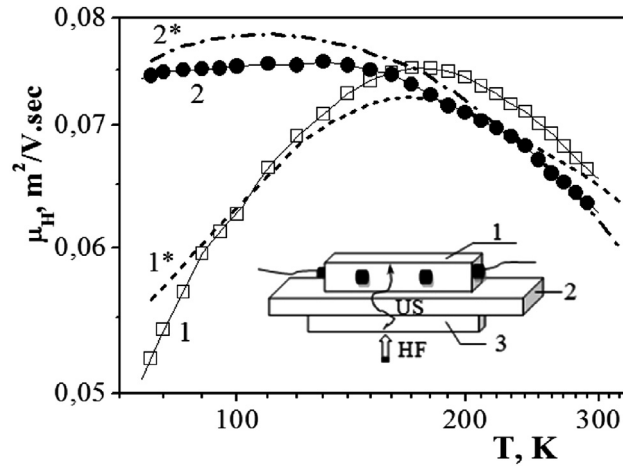


Fig. 2. CdTe:Cl. Temperature dependence of electron mobility. Experiment: light point – without US; black point – US influence $W_{US} \approx 2 \cdot 10^4 \text{ Wt/m}^2$. Calculation: Curve 1* – calculated taking into account the scattering by thermal vibrations of the crystal lattice and ionized impurity ($N_I = 7.6 \cdot 10^{23} \text{ m}^{-3}$); curve 2* – calculated taking into account the scattering by thermal vibrations of the crystal lattice, ionized impurities ($N_I = 5.0 \cdot 10^{23} \text{ m}^{-3}$) and the piezoelectric potential. In insert is the scheme of acoustic box: 1 – sample, 2 – buffer, 3 – piezoelectric transducer; HF – high frequency; US – ultrasound.

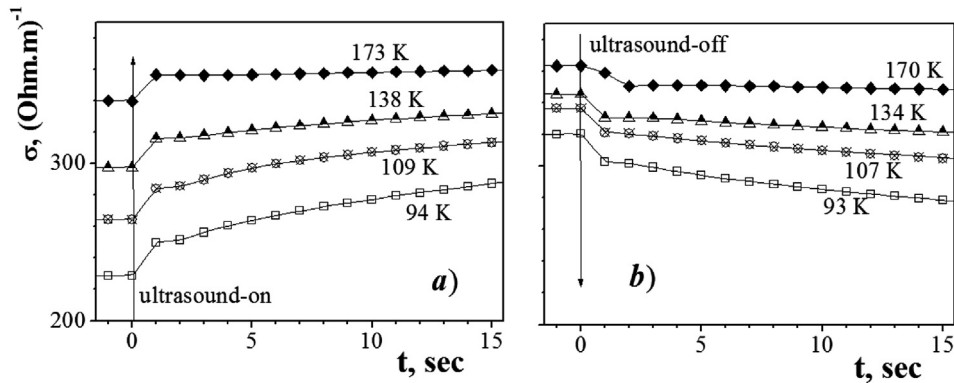


Fig. 3. CdTe:Cl. Time dependence of the electrical conductivity at different temperatures when ultrasound-on ($W_{US} \approx 2 \cdot 10^4 \text{ Wt/m}^2$) (a) and when ultrasound-off (b), respectively.

isolated point defects Cl_{Te}^+ [9]. Slight temperature changes $n_e(T)$ and slight increase at low temperatures under the **US influence** can take place due to the change of Hall factor because of dependence of its value on the mechanism of scattering and **additional electrons release from metastable acceptor defects into the neutral state by the AS transition also (see below)**. Note that $n_e(T)$ both in the initial sample, and under the US influence in all temperature range measurement depends on the temperature weakly, that is typical for the depletion region of impurity donor level, ionization of which is responsible for the formation of free electrons in CdTe conduction band [10].

3.2. Temperature dependence of carrier mobility

Fig. 2 shows the temperature dependence of electron mobility $\mu_H(T)$ both at the absence of US influence (curve 1) and under US loading (curve 2). The figure shows that the distribution of **US waves** in a crystal greatly affects $\mu_H^{US}(T)$ at **low temperatures, leading to significant increase μ_H** . On the contrary, at the temperature close to room one, under the US influence some **μ_H reduction can be observed**. It is necessary to note that given results correlate well to research data of US influence on $\mu_H(T)$ in crystals HgCdMnTe [11,12]. It must be emphasized that the amplitude of mobility are low, it usually evidences about the significant contribution of the charge carrier scattering on inhomogeneities in the crystal caused by clusters of impurities [13,14]. The question of the observed scattering in our samples should be considered and researched additionally. In this paper to estimate the quality of US influence on IDS crystal there formally was used the classical model of the homogeneous semiconductor.

Taking into account the experimental dependence 1 there can be seen two different temperature regions $\mu_H(T)$, that in general, corresponds to the main mechanisms of carrier scattering in semiconductors [10]. At **low temperatures ($T < 150 \text{ K}$) ionized impurity scattering** is predominant, and at the temperature close to room one (**$T > 180 \text{ K}$**) – the thermal vibrations of

the crystal lattice. Indeed, taking into account these two mechanisms of scattering we can quite satisfactorily describe the experiment $\mu_H(T)$ (Fig. 2, curve 1*). The best coincidence of experimental and calculated curves 1 and 1* can be observed when we use $n_e \approx 2.7 \cdot 10^{22} \text{ m}^{-3}$ та $N_I^0 \approx 7.6 \cdot 10^{23} \text{ m}^{-3}$ (N_I —concentration of ionized impurities in the Brooks-Herring models).

Curve 2, obtained by US loading. At high temperatures ($T > 150 \text{ K}$) character of $\mu_H^{US}(T)$ does not change, there can be seen only a slight decrease $\mu_H^{US}(T)$. At the same time at low temperatures ($T < 140 \text{ K}$) under the US action there can be observed an increase $\mu_H^{US}(T)$, which is almost independent of temperature. It means that at US influence the definite change of the main mechanisms of carrier scattering takes place. For satisfactory adjustment of the calculated curve 2* with experimental dependence 2 at high temperatures ($T > 200 \text{ K}$) calculated $\mu_H^{US}(T)$ with the formal involvement of additional scattering on the piezoelectric potential ($\mu_{ph} = AT^{-1/2}$, where A —some effective coefficient that does not depend on the temperature, selected) allowed to get satisfactory figures of the calculated curve 2* with experimental 2. Note that a A -coefficient exact calculation for the case of US perturbed crystal phonon system is impossible. For low-temperature region ($T < 150 \text{ K}$) scattering on ionized impurity and in the case of US action is considered to be predominant. Thus, the selected concentration of scattering centers was $N_I^{US} \approx 5.0 \cdot 10^{23} \text{ m}^{-3}$. Comparing the chosen values of concentrations of ionized impurities in the initial sample ($N_I^0 \approx 7.6 \cdot 10^{23} \text{ m}^{-3}$) and at US loading ($N_I^{US} \approx 5.0 \cdot 10^{23} \text{ m}^{-3}$) we can speak about AS restructuring of point defects ($\Delta N_I = N_I^0 - N_I^{US}$). It is the most likely to assume that reduce N_I^0 , while maintaining a nearly constant value of carrier concentration (according to Fig. 1 $\Delta n = n_{US} - n_0$ is not exceeding $5 \cdot 10^{21} \text{ m}^{-3}$), takes place mainly due to the formation of neutral complexes at US influence involving electrically-active centers of the donor and acceptor type. This additional scattering by neutral complexes formed at US does not compensate the scattering change efficiency by decreasing the concentration of N_I .

3.3. Relaxation processes of conductivity at US switching-on as well as at US switching-off

Fig. 3 shows the time dependence of conductivity change $\sigma(t)$ of the sample for different temperatures. Character of relaxation $\sigma(t)$ under the US influence and without it is reversible. Relaxation duration slightly in-creases with decreasing of sample temperature and shows long-term AS mechanism of IDS crystal rebuilding. And, as it was already noted above, even long-term US loading of the sample does not lead to the residual changes of the parameters of crystal. More detailed examination shows that the relaxation $\sigma(t)$ is not monotonous generally, but, at least, has two stages. Indeed, at the time of US-on(-off) initially a jump change of $\sigma(t)$ takes place, which later becomes monotonous long-term relaxation. Approximate evaluation of duration of the first stage give $\tau_1 < 1.0 \text{ sec}$. At the same time the duration of the second stage τ_2 is (50÷500) sec. Two-stage nature of the AS time changes of EPh parameters in CdTe:Cl indicates two mechanisms of IDS crystal rebuilding. We think that acoustic active metastable defects are responsible for “instantaneous” jump-like changes $\sigma(t)$, which are $\sim(10\div20)\%$ of the total change σ . These defects where different configurations of the lattice correspond to different charge states and which are separated from each other by a potential barrier. Thus, in CdTe:Cl there are considered complexes $[V_{Te}-Cl]$ [2,13–15]. At the same time, we think, diffusion AS processes are responsible for the long-term $\sigma(t)$ relaxation in which the defining role belongs to dislocations. There can be the processes of “capture” or “release” of moving electrically active point defects with dislocations [5,6,12]. There can be accelerated diffusion of individual point defects along (or in the neighborhood) of dislocations that intensively vibrates under US influence.

The problem requires further studying. However, given below numerical estimations based on EPh parameters calculations of our experimental data prove this model. Let us remind that the total concentration of N_{Cl}^0 in the melt was $\approx 1 \cdot 10^{24} \text{ m}^{-3}$. We think that the distribution of the doped impurities between defect complexes containing Cl atoms, is the following: a) part of Cl atoms creates an isolated point defect Cl_{Te}^+ , that mostly determines the level of donor $N_D(E_C - 0.01 \text{ eV})$ [3]; b) part of Cl atoms is located on the acceptor $[(V_{Cd}^- Cl_{Te}^+)]$ and neutral $[(V_{Cd}^- 2Cl_{Te}^+)^0]$, $[(V_{Cd}^- Cl_{Te}^+)^0]$ complexes N_A ; c) part of Cl atoms is captured by the dangling bonds on the dislocations N_{Cl}^{dis} . That is:

$$N_{Cl}^0 \approx N_D + N_A + N_{Cl}^{dis} \quad (1)$$

We can suppose that the main mechanism of AS IDS rebuilding is Cl atom joining to acceptor complex:



As a result of this AS chemical reaction the ionized impurity concentration decreases as it was shown above (see 3.2) on $\Delta N_I = N_I^0 - N_I^{US} \approx 2.6 \cdot 10^{23} \text{ m}^{-3}$. Thus, for realization (2) we still need the same number of Cl atoms. As n_e at US loading actually does not decrease, and even slightly increases, it is necessary to search other sources of these Cl atoms. We think that the dislocations can be such source and $N_{Cl}^{dis} = \Delta N_I \approx 2.6 \cdot 10^{23} \text{ m}^{-3}$, respectively. Then, taking into account that in the initial sample $N_I^0 = N_D + N_A \approx 7.6 \cdot 10^{23} \text{ m}^{-3}$, and $n_e = N_D - N_A \approx 2.7 \cdot 10^{22} \text{ m}^{-3}$, we find that $N_D \approx 3.9 \cdot 10^{23} \text{ m}^{-3}$ and $N_A \approx 3.7 \cdot 10^{23} \text{ m}^{-3}$. Thus, compensation degree is $N_A/N_D \approx 0.93$. According to (1) we obtain: $N_{Cl}^0 \approx 10^{24} \text{ m}^{-3}$, that corresponds to the given initial of the doped concentration.

While switching-off the US loading there must be observed the reverse process, since the probability of formation of acceptor complex $[(V_{Cd}^- Cl_{Te}^+)^-]$ in equilibrium state (US-off) is much larger than $[(V_{Cd}^- 2Cl_{Te}^+)^0]$.

4. Conclusions

There have been found out long-termed acousto-stimulated changes of electro-physical parameters in crystal CdTe:Cl, that can be seen only during the US influence. Analysis of the temperature characteristics of concentration and Hall mobility of electron carriers showed that the main mechanisms of carrier scattering in the initial samples are scattering on thermal vibrations of crystal lattice and ionized impurities; and with US influence in crystals additional carrier scattering on piezo-electric potential and oscillating dislocations takes place. Two-stage nature of the AS change in EPh parameters in CdTe:Cl indicates two mechanisms of IDS crystal rebuilding. And acousto-active metastable defects are responsible for “instant” jump-like changes $\sigma(t)$. At the same time AS diffusion processes where the defining role belongs to dislocations, in the results of which a transformation of the charged acceptor complexes $[(V_{Cd}^{2-}Cl_{Te}^{+})^-]$ into neutral $[(V_{Cd}^{2-}2Cl_{Te}^{+})^0]$ takes place, are responsible for long-term relaxation $\sigma(t)$.

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