Changes in the Electrical Parameters of CdTe-based Crystals During Isothermal Annealing

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Abstract—We observed a novel unanticipated effect in CdTe, $Cd_{1-x}Zn_xTe$ and $Cd_{1-x}Mn_xTe$ crystals whilst we were measuring the dependences of several electrical properties (e.g., specific conductivity and free-carrier density) over time. During isothermal annealing under constant thermodynamic conditions (temperatures of 450-500°C and under maximal cadmium-vapor pressure), we recorded a jump-like increase in the conductivity after some $\sim 1 - 2$ hours of heating required to stabilize the sample's electric parameters. The values of specific conductivity and free-carrier density suddenly increased by up to tenfold, and they persisted at those levels during further ageing. At the same time, the sample's conductivity became insensitive to stoichiometric changes in the crystal. We explain this effect as reflecting a sudden reformatting of the sample's native/foreign point-defect structure. This transformation is evaluated and mathematically approximated within the framework of our model of the melting of Te-containing second-phase particles; this process releases impurities from within the particles. The respective diffusion "clouds" grow, and at the moment of their mutual percolation (infiltration), a peculiar "short circuit" is observed with striking changes in the crystals' electrical parameters.

Index Terms—Annealing, $Cd_{0.9}Zn_{0.1}Te$, component over-pressure, crystals, inclusions.

I. INTRODUCTION

SINGLE crystals of cadmium telluride, mainly $Cd_{1-x}Zn_xTe$, are widely used as room-temperature detectors of ionizing radiation [1]–[3]. Their sensitivity primarily depends upon the nature and concentration of native/foreign point defects (NPDs/FPDs) in the material [4]–[6]. The NPD content is determined by the thermodynamic parameters to which the crystal was exposed, i.e., temperature and stoichiometric relations, defined by the components' vapor pressures in the ampoule. However, these relationships fit only at high-temperature point-defect equilibrium (HTDE). Therefore, the best method of exploring the spectra of the point defects is by conducting high-temperature (over $\sim 400°C$) "in situ" electrical measurements [7]–[9].

Furthermore, the nature and density of the second-phase particles (SPPs) in a single crystal body are important in determining the material's properties. The SPPs are composed mainly of polycrystalline tellurium containing varied and uncontrolled amounts of impurities. Their provenance may differ: the precipitates evolve from the precipitation of excess tellurium in the crystal during cooling, while the inclusions are due to the incorporation of microscopic drops of the Te-rich melt at the crystallization front of the growing crystal. The size and density of the SPPs can be evaluated via infrared transmission microscopy. As the presence of SPPs in the single crystals lowers the detector's energy resolution, methods of eliminating them have been sought. High-temperature annealing of the crystals in atmospheres of different vapors usually is employed [10]–[12]. However, until now, mostly structural changes (removal of inclusions) in the crystal were considered. It has become evident that some re-organizing of the crystal's impurity distribution and its influence on electrical properties also should be taken into account. Such knowledge would facilitate the task of obtaining material with desired electric properties and uniformity.

II. EXPERIMENTAL

Single crystals of CdTe, $Cd_{1-x}Zn_xTe(x = 0.04 - 0.10, CZT)$ and $Cd_{1-x}Mn_xTe(x \sim 0.05, CMT)$ were grown by the conventional Bridgman method in graphitized ampoules. In some cases, a small amount of indium was introduced, such that its concentration in the crystal did not exceed $(3 - 5) \times 10^{16}$ atoms/cm^3. The total content of uncontrolled electrically active impurities was estimated to be in the 10^{16} atoms/cm^3 range. In addition, we investigated crystals grown in other laboratories. All the grown ingots were cut into samples with a dimension of 2.5 mm $\times$ 2.5 mm $\times$ 12 mm for electrical measurements, then polished and etched in a methanol-bromine solution. Before the annealing experiments, the samples had the following properties: CdTe–p-type conductivity, specific conductivity $\sigma \approx 10^{-4} - 10^{-5} (\text{Ohm·cm})^{-1}$; $Cd_{1-x}Zn_xTe$ – p- or n-type conductivity, $\sigma \approx 10^{-9} - 10^{-10} (\text{Ohm·cm})^{-1}$; and, $Cd_{1-x}Mn_xTe$ – p- or n-type conductivity, $\sigma \approx 10^{-8} - 10^{-9} (\text{Ohm · cm})^{-1}$.
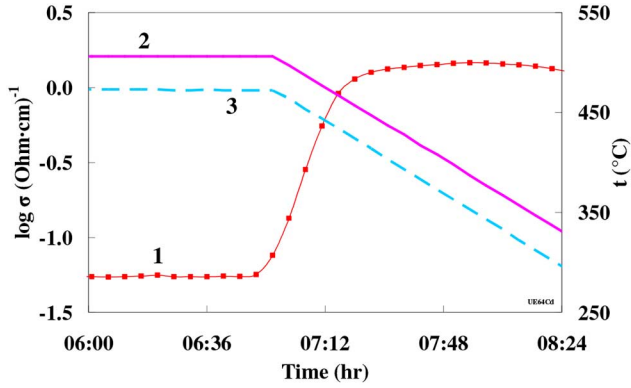
Fig. 1. Sudden specific conductivity "jump" after 1-hour annealing at $500°C$ in the undoped CdTe (sample UE64Cd). 1–conductivity;2–CdTe temperature; 3 - Cd temperature.

Using the method of capacitor discharge, six contacts were welded to the samples for our measurements of their conductivity and their Hall effect. The samples were placed in the ampoule for high-temperature electrical measurements, together with a small charge ($\sim$ 200 mg) of the component that defined the sample's non-stoichiometry at the HTDE. The ampoules were evacuated to 10^{-4} mbar and pressurized. We earlier described our techniques [8] for obtaining automatic computer-assisted high-temperature electrical measurements (i.e., the processes for determining values for the specific conductivity, free carrier density, and mobility).

III. RESULTS

We annealed CdTe-based crystals of different chemical composition under "in situ" control of their electrical properties to explore possibilities of improving their resistivity. In so doing, we observed an unusual effect in almost all those samples annealed under Cd saturation. Heating the sample at a constant temperature of around $500°C$ and under maximal cadmium vapor pressure $P_{Cd,max}(t_{Cd} = t_{CdTe} - 10\ K)$, we noted that the electrical parameters which had remained stable over $\sim 1 - 2$ hours manifested a sudden significant increase (a "jump", referred to hereafter as the "effect") in both specific electrical conductivity and free-electron density. Figs. 1–6 show the most representative data. Here and further on, the upper line (1) in the graph corresponds to the sample's temperature, and the lower one (2) to the component's zone. The letters "Cd or Te" in the figure's code name describe the chemical nature of the dominant vapor component in the ampoule ($P_{Cd,max}$ or $P_{Te2,max}$, correspondingly), whereas "CdTe" or "Cd(Zn)Te" represents the mean conditions of the compound's congruent sublimation (c.s.), i.e., $P_{Cd,c.s.}$.

We note in Fig. 1 that the post-effect decline in temperature does not alter the value of specific conductivity. In Fig. 2, the effect is evident as soon as $500°C$ is reached. The "[e$^-$] jump" in Fig. 3 is observed only after the sample has attained $480°C$. Subsequent step-wise cooling of the sample to $400°C$ does not affect its conductivity.

Annealing the samples at $400-$ and $430°C$ does elicit this effect (Fig. 4). Under those conditions, the temperature differences strongly influence the conductivity, but only at $460°C$
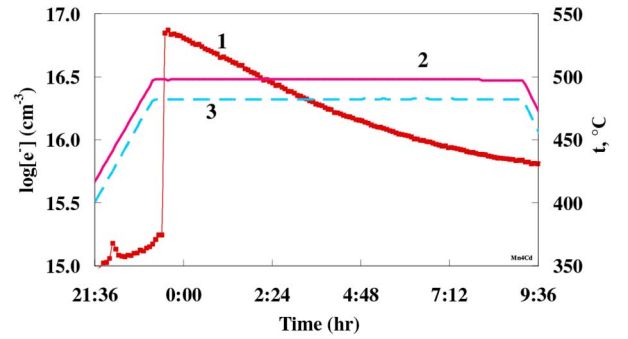

Fig. 2. The effect in the Cd(Mn)Te (sample Mn4Cd).1–electron density; 2–CdTe temperature; 3–Cd temperature.
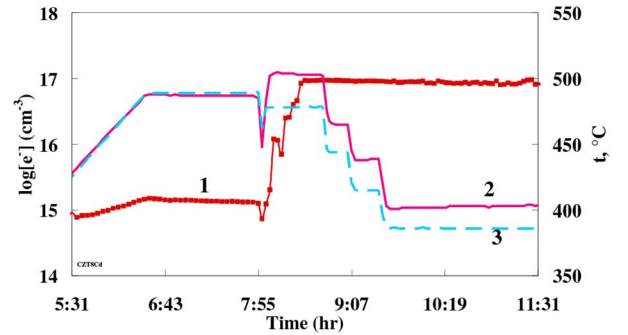

Fig. 3. The effect at P_{Cd} in the sample CZT8Cd. 1–electron density;2–CdTe temperature; 3–Cd temperature.

does the effect become apparent, whereupon the σ temperature-dependence disappears.

In parallel to the experiments under P_{Cd}, we undertook a series of experiments with different atmospheres in the ampoules - either P_{Te2} or $P_{Cd,c.s.}$ conditions. For this purpose, we used crystals in which the effect of the annealing in a Cd-vapor atmosphere previously had been observed.

In Figs. 5 and 6, the effect is hardly visible though its outcome is apparent, viz., the retention of stable values for the specific conductivity when the temperature is lowered.

IV. DISCUSSION

We undertook a series of 60 experiments, using different crystals, temperatures, and vapor atmospheres during annealing, which allowed us to specify the main features of the "effect". The following findings were extracted from the data sets:

1. The effect is observed in 80-90% of the investigated samples of CdTe, CZT, and CMT that were annealed under P_{Cd}, max conditions.
2. Generally, the effect occurs when the sample is annealed at a temperature above $470-500°C$. In individual cases, the effect begins at temperatures ranging from $400-450°C$ and rarely, its onset occurs at slightly above $500°C$.
3. The annealing time necessary to reach the effect varies between about 1-2 hours in different samples.
4. In the post-effect time range, variations in the stoichiometry (P_{Cd} changes) do not affect the materials' main electrical properties, indicating an impurity-controlled mechanism of conductivity (Figs. 1, 3, and 4).
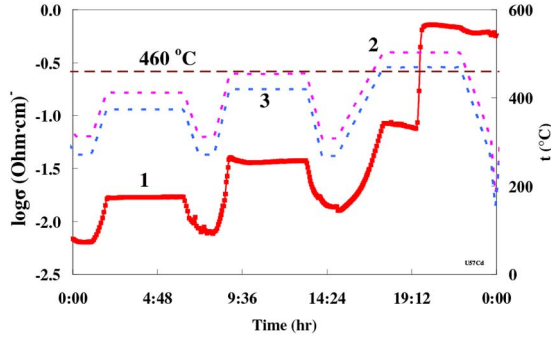
Fig. 4. The effect at $P_{Cd,max}$ in the undoped CdTe (sample U57Cd).1–conductivity; 2–CdTe temperature; 3–Cd temperature.
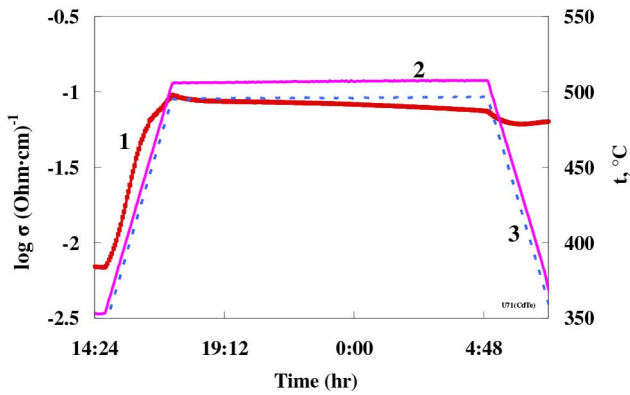

Fig. 5. Conductivity-time dependency in CdTe at $P_{c.s.}$.(sample U71CdTe): 1–conductivity; 2–CdTe temperature;3–Cd temperature.
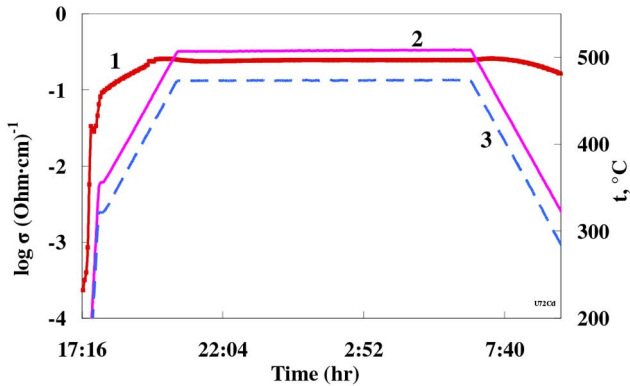

Fig. 6. Conductivity-time dependency in Cd(Zn)Te at P_{CdTe}. (sample CZT29Te):1–conductivity; 2–Cd(Zn)Te temperature; 3–CdTe temperature.

5. Infrared transmission microscopy shows that even after durable sample annealing and the "effect" occurrence (up to 48 hours of annealing at $500°C$), the SPPs still are visible.

6. Repeated electrical properties-time measurements during cooling-heating experiments did not reveal any changes in the effect.

7. Annealing under Te vapor pressure or under CdTe (CZT) c.s. conditions prevent the change in conductivity.
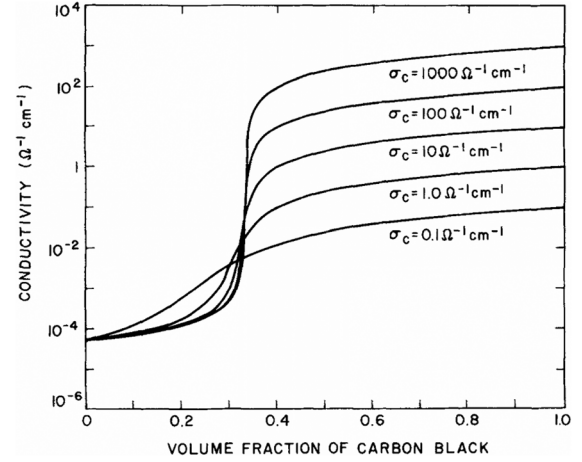

Fig. 7. Specific conductivity of plastic-graphite composites as function of the graphite volume-fraction at different relations between the conductivities of the two components (modeling using Bruggeman's formula [13]). The conductivity "jump" (percolation limit, short circuit) happens around a value of 0.33 graphite volume fraction. In real experiments, a 0.35 value was obtained [15]. Reproduced with permission from "Electrical permittivityand conductivity of carbon black-polyvinyl chloride composites",K. T. Chung, A. Sabo and A. P. Pica, J. Appl. Phys. 53, 668 (1982). Copyright 1982, AIP Publishing LLC.

V. THEORY AND CALCULATIONS

A. Theory

All single crystals we investigated (e.g., CdTe, CZT, and CMT) contain precipitates/inclusions of a second phase. We note the undoped CdTe samples used in the measurements were grown at the Chernivtsi National University laboratory, and others were obtained from other laboratory's crystals, often slightly doped with indium. At the beginning of the annealing after reaching the HTDE, the free-carrier density was (under Cd vapor pressure) around 10^{15} cm^{-3} and remained unchanged some 1-2 hours; then, that was followed by onset of the effect, with a fast rise in the density of free electrons reaching values substantially exceeding some $\sim 10^{16}$ cm^{-3} (Fig. 7), an increase of approximately ten-to-fifty fold. This event can be explained only by a sudden similar rise of the content of electrically active donors (n-type conductivity). The different impurities in the SPPs, mentioned above, were mostly metals. To all appearances they existed in either an atomic form or bound in a respective telluride state (e.g., electrically inactive). These impurities are immobile in SPPs, because at temperatures (below $451°C$), tellurium is solid; however, at temperatures exceeding onset of the effect, the impurities become mobile due to SPPs melting. Such considerations form the basis of the following model of the Te particles' behavior in all of the CdTe-based compounds that we explored.

Our basic assumption is that the processes in isothermally annealed CdTe, CZT, CMT are similar to those to which the classical electro-conductivity of inhomogeneous solids theory has been applied (since 1928). This theory allows us to calculate the time of so-called "percolation"/"infiltration", at which moment a sharp increase of the sample's conductivity is observed. Omitting different formulae for calculating the numerical relations between the critical volume-fractions of the two phases [13][14], we analyze the results of an interesting tangential in-

vestigation [15]. Its goal was to assess the maximal amount of graphite powder that is admissible in a filled white plastic (a material for cars' dash boards) to obtain a black coloration whilst retaining the insulator properties of the dielectric plastic. Fig. 7 shows the results.

A comparison of data in the literature about the electro-conductivity of inhomogeneous solids with our experimental results concerning the "effect" supports our proposing the following model of the SPP's behaviour during crystal annealing.

As stated, the SPPs contain substantial amounts of different impurities. At temperatures reaching/exceeding the melting point of tellurium, i.e., $451°C$, the SPPs melt, and the now mobile impurities begin to diffuse out of the liquid; the same can happen with impurities bound in tellurides, as the latter dissolve in molten tellurium where they can dissociate, so releasing the impurities to diffuse into the crystal's volume.

The out-diffusion of predominantly metal atoms/ions occurs at different velocities, conforming to the diffusion coefficients of the atoms/ions. In such a manner, around each SPP a particular diffusion "cloud" untwists, filled by atoms/ions of different nature (and different electrical behaviour). Over time, these "clouds" continuously grow due to the progressive diffusion, until the clouds begin to "touch" one another. The first such contact is random (depending on the SPP's size and distribution and the components' diffusivities), but when these events become predominant, it triggers a short circuit (the percolation limit is reached), and the sample's conductivity sharply rises (similarly to Fig. 1, in our experiments–the "effect"). Now, the higher conductivity of the crystal is caused by foreign PDs, rather than by native PDs, so it no longer depends on temperature changes and/or stoichiometric relations (i.e., its insensitivity to P_{Cd} variations) in the solid (Figs. 1, 3, 4). We note the difference in the treatment of the subject by the theory of conductivity of inhomogeneous solids, compared to that in our case. The former treats the conductivity changes in the course of the growth of the volume fraction of the more conductive particles, whereas the latter encompasses the growth only of an invariable quantity (equal to the amount of SPPs) of diffusion "clouds". However, both models result in the same outcomes–percolation and a dramatic growth in the specific conductivity.

VI. CALCULATIONS

The simplest way to evaluate the reliability of this model is to estimate the time necessary to achieve the percolation limit (t_{crit}), and to compare it with the experimental values. This is not a simple task, taking into account the differences in the SPPs' size, form and density, their usually irregular distribution in the crystals' volumes, the differences between the diffusion coefficients of various impurity atoms, and other features.

The task can be simplified assuming, in a rough approximation, that all SPPs initially are regularly distributed spheres with an averaged diameter "d" in cm, "t_{crit}" is the effect's appearance time in seconds, "D" is the effective impurities' diffusion coefficient in cm^2/s, and "V_{sum}" is the total SPP particles' volume per cm^3.

This leads to the following formula (1),

$$t_{crit} = d^2/25D(V_{sum})^{2/3} \qquad (1)$$

Assuming that,
- $d = 10^{-4}$ cm or 1 μm (median value between 0.1 and 10 μm);
- Percent volume of SPPs $= 10^{-4}\%$; $V_{sum} = 10^{-6}$ cm^3 (as in [17]);
- $D = D_{In}$ at $500°C(1.6 \times 10^{-10}$ cm^2/s)[18].

Then, we obtain, $t_{crit} = 3.4$ hours, which coincides fairly well with most of our experimental percolation times–i.e., 1-2 hours.

Now, we consider some unusual features in our experimental data and test their explicability in the framework of our proposed model.

1. In some investigations with CdTe, CZT, and CMT (mostly obtained from other laboratories), the effect was not observed even after 2-3 days of prolonged annealing at $500°C$. Seemingly, such crystals were thermally treated during possible post-growth cooling/annealing procedures at sufficiently high temperatures that altered their second-phase structure by removing or extracting the impurities already there. We observed the same in our samples annealed to remove the second phase; in repeated experiments, the effect was absent.

2. In some (rare) experiments, the effect was observed as early as at $\sim 400°C$, i.e., lower than the melting point of Te. In the framework of the model, we explained this as follows: In these crystals, the local related Te/tellurides were close to those in their respective eutectics but lower than that for the melting temperature of pure Te. In contrast, in some experiments, the effect occurs at temperatures substantially higher than the Te melting point, viz., around $550°C$. Here, it can be supposed that, by chance, metal tellurides with higher melting points can also be present in the SPPs, and that they do not fully release their components at lower annealing temperatures (e.g., 460-500°C).

3. The practical absence of a pronounced effect in crystals annealed both under Te saturation or compound c.s. conditions can be explained as follows. Crystal annealing under Cd saturation generates a lot of donor atomic NPDs and, correspondingly, electrons (in the 10^{15} cm^{-3} order-of-magnitude at $500°C$). In this effect they join the electrons, appearing at the ionization of FPDs released by the SPPs. Therefore, the total electron density rises considerably, and the effect is observed readily. In Te-saturated crystals or those treated under c.s. conditions, the acceptor NPDs dominate. The latter compensate (more or less) for the electrons, generated by the ionization of FPDs during the effect, and hence, the crystal's conductivity changes insignificantly.

Nevertheless, the observed effects and the model we have proposed enlarge our knowledge of SPPs transformations occurring at moderately high-temperature crystal annealing. Until now, mostly structural changes (SPP removal) in the crystal

were considered, and it has become evident that some re-organizing of the crystal's impurity distribution and internal electric field also should be considered. Such knowledge would facilitate the task of obtaining material with desired electric properties.

In discussing the proposed model of SPP's transformation during crystal annealing, it is worthwhile to compare it with a somewhat different model. In [17], [18] Cd(Zn)Te crystals were annealed some tens of hours under $P_{Cd,c.s.}$ at 450-500°C, after which time they were quickly cooled to 20°C. In low-temperature (liquid nitrogen) Hall-effect measurements, a substantial rise in free-carrier mobility was observed, probably due to the essential diminution of both free donors and acceptors ("self-purification" effect). The latter was explained by assuming that at the annealing temperatures the molten SPPs (tellurium) absorb the free impurity particles, so diminishing their content in the surrounding crystal. In the framework of our model of the "conductivity-jump" effect, the "self-purification" effect can occur owing to the formation at very low temperatures of more-or-less stable donor-acceptor pairs, thus diminishing the density of scattering centers.

VII. CONCLUSIONS

1. For the first time in CdTe−, $Cd_{1-x}Zn_xTe$−, and $Cd_{1-x}Mn_xTe$-crystals, we observed a jump-like increase of the specific conductivity versus time during long-time annealing.

2. That effect was explained by assuming the transformation of second-phase particles in the crystals, similar to the percolation phenomenon in two-phase solids with different conductivities.

3. This jump-like increase in the free-carrier density occurs due to the melting of the second-phase particles, thereby releasing additional donor impurities that were concentrated in the second-phase particles into the crystal's matrix. The role of impurities in the conductivity is confirmed by the independence of the sample's electrical parameters after specific temperature/stoichiometric changes.

4. A calculation of the time necessary to obtain the percolation effect resulted in acceptable values, in accord with the experimental observations.

5. The results and their calculated estimations provide a deeper insight into the mechanism of second-phase particle transformations during the annealing of CdTe, ($Cd_{1-x}Zn_xTe$− or $Cd_{1-x}Mn_xTe$) crystals, which can

be useful in developing improved procedures to obtain high-resistivity detector-grade material that is free of SPPs.

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