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Electrical Instability of CdTe:Si Crystals

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Results of Hall effect measurements of cadmium telluride crystals, doped by silicon (dopant concentration in the melt was $10^{18} - 10^{19} \text{ cm}^{-3}$), allowed to classify the studied samples and the conditions under which probably the definite crystal and impurity states are realized. We have found the distinction between 3 type of CdTe:Si crystals: (1) low-resistance p-type crystals with shallow acceptors, in which Si impurity is localized mainly in the large inclusions; (2) semi-insulating crystal with deep acceptors and submicron size dopant precipitates that are source/drain for interstitials Si_i - shallow donors; and (3) low-resistance crystals in which the n-type conductivity is provided by shallow donors: Si_i (and/or Si_{Cd}). Therefore the silicon is responsible for n-type conductivity of doped samples, introducing as a donor Si_i and provides semi-insulating state by forming deep acceptor complexes ($\text{Si}_{\text{Cd}} \text{V}_{\text{Cd}}^{2-}$) with ($E_v + 0.65 \text{ eV}$). Besides, the submicron silica precipitates, that have a tend to "dissolution" at relatively low temperatures, can act as electrically active centers.

Keywords: cadmium telluride, silicon, doping, electrical properties, impurity, precipitates.

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Introduction

In CdTe crystals, grown from the melt in quartz containers, silicon impurities very likely are present. Its content sometimes reaches 10^{18} - 10^{19} at/cm^3 , which is substantially higher in comparison to other uncontrolled impurities [1-3]. However, definite conclusions concerning the electrical activity of this impurity in CdTe crystals are absent. In particular, in [4] it was not observed significant differences in the electrical properties of CdTe:Si and undoped CdTe crystals, grown under similar conditions. At the same time, attention is drawn to a high yield of n-type material that is unusual for undoped crystals. Note, that the photoluminescence [4] and cathodoluminescence spectra [5] for the undoped and silicon doped crystals differed substantially for samples from different portions of a single crystal. Some information about CdTe:Si crystal properties was published in [6-7], however the results do not match those of previous works. deals with CdTe:Si crystals electrical properties. This discrepancy in the results requires further investigations of CdTe:Si crystals.

I. Experiment

CdTe crystals were doped by Si (dopant concentration in the melt $C_0 = 10^{18} \div 10^{19} \text{ cm}^{-3}$) and grown in graphitized quartz ampoules by the vertical Bridgman method.

The temperature dependences of the Hall coefficient R_H and $n = 1/eR_H$ electrical conductivity σ , and hence carrier concentration (n) and mobility (μ) in samples cut from different parts of the CdTe ingot were investigated.

The measurements were performed both in low-temperature (LTM) ($T = 77 \div 420 \text{ K}$) (Fig. 2, 3), and in high-temperature (HTM) regions ($T = 520 \div 1250 \text{ K}$) (Fig. 4, 5). At high-temperature the investigation were performed under Cd-saturated overpressure in 2-zone furnace [8]. Photoexcitation of the samples was ensured by monochromator IRS-12. IR images of second phase were obtained using Leitz microscope with IR camera Pixelink PL-A741.

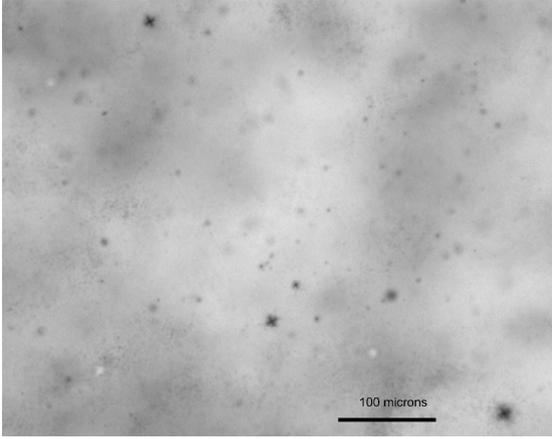


Fig. 1. The common distribution of small and large inclusions in CdTe:Si sample.

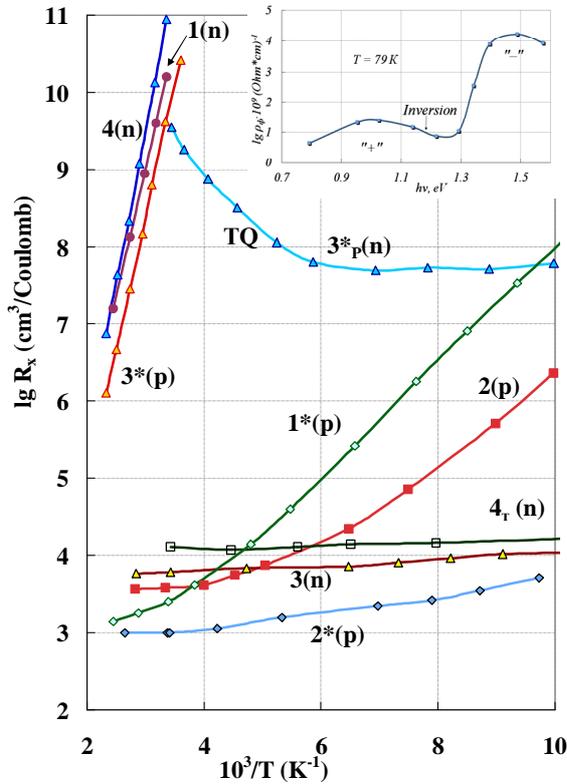


Fig. 2. The temperature dependence of the Hall coefficient in the samples, cut from different parts of the ingot ($g=x/L$, where x – axial coordinate, L – the length of the ingot) with different concentration (C_0) of Si dopants in the melt: $C_0 = 10^{18} \text{ cm}^{-3}$; $1-g = 0.11$; $1^* - g = 0.93$; $C_0 = 2 \cdot 10^{18} \text{ cm}^{-3}$; $2-g = 0.13$; $2^* - g = 0.5$; $C_0 = 3 \cdot 10^{18} \text{ cm}^{-3}$; $3-g = 0.2$; $3^* - g = 0.6$; 3^*_p – with its intrinsic photo-excitation; $C_0 = 10^{19} \text{ cm}^{-3}$; $4-g = 0.3$; 4_r – after STT. Near the sample's number their conductivity type

II. Results and discussion

The LTM results evidenced that all investigated samples can be divided into three groups:

1 - low-resistance p-type samples (curves 1^* , 2 , 2^* in

Fig. 2), in which conductivity is determined by the acceptors $A1$ ($E_V+0.05 \text{ eV}$) or $A2$ ($E_V + 0.12 \div 0.14 \text{ eV}$);

2 - high-resistance samples of p-and n-type (lines 1, 3^* , 4), the conductivity of which is determined by the A-acceptors ($E_V+0.65 \text{ eV}$) or the donors D ($E_C - 0.6 \div 0.7 \text{ eV}$);

3 - low-resistance samples (curves 3, 4_r^*) with n-type donors $D1$ ($E_C-0.01 \text{ eV}$). The carrier mobility (Fig. 3) in the samples of groups 1 and 3 is controlled by traditional scattering mechanisms: on optical lattice vibrations and on ionized impurities. At the same time for the samples of group 2 (curves 1 and 3^* , 4) the temperature dependence of the mobility is exponential:

$$\mu = \mu_0 \cdot \exp(-\epsilon_b/kT),$$

which is typical for crystals with drift barrier height ϵ_b [9]. Heating of such samples during measurement (at $T > 373 \text{ K}$) is accompanied by isothermal increasing of carrier mobility and decreasing of barrier drift height. Moreover short temperature treatment (STT: $T=1073 \text{ K}$; $t=1 \text{ min.}$) and HTM are accompanied by such radical changes in the defect-impurity system state (DIS), that the samples “move” to the group 3 with an electron concentration $n \sim 10^{15} \div 10^{16} \text{ cm}^{-3}$. When storing these samples (at room temperature) a slow relaxation of the carrier density and mobility to state of the group 2 samples is observed.

At intrinsic photoexcitation ($h\nu \sim E_g$) the samples of 2nd group show ($T < 300 \text{ K}$) an electronic photoconductivity with temperature quenching (curve 3^*_p in Fig. 2). At the same time in the spectral photoconductivity dependence at $T=79 \text{ K}$ (see inset in Fig. 2) and $h\nu < 1.2 \text{ eV}$ the electron photoconductivity is replaced by the hole one.

It is known that the electrical parameters of CdTe ingots, obtained by the Bridgman method and doped by Ge, Sn impurities during the growth [10], are forecasted, reproducible and go into the range of 2-3 orders of magnitude in the carrier density. Herewith the conductivity is controlled by deep centers with levels located near the middle of the forbidden gap. At the same time CdTe-Si crystals, grown under similar conditions, exhibit a wide range of electrical parameters values: conductivity type, charge carrier density, mobility and the nature of their temperature dependence.

The reason for such differences can be found in different incorporation character of Si into the crystal matrix, on the one hand, and Ge, Sn, on the other hand. First, the Ge and Sn segregation coefficients in cadmium telluride are substantially less than unity. Therefore these impurities (at enough temperature gradient at the crystallization front) are “pushed” to the top of the ingots and there the impurity phase division is observed, due to the limited solubility of these impurities. At the same time, the segregation coefficient of Si impurity in CdTe is close to unity (exceeds a little). It means that during the doped crystal growth the impurity has to be evenly distributed along the ingot or to be slightly pushed in the lower part of the ingot.

It is clear that if we used the values $C_0 \geq 10^{18} \text{ cm}^{-3}$ all the amount of the Si impurity can not dissolve in the solid phase. And so at the crystallization front impurity inclusions of a wide size range are formed [9].

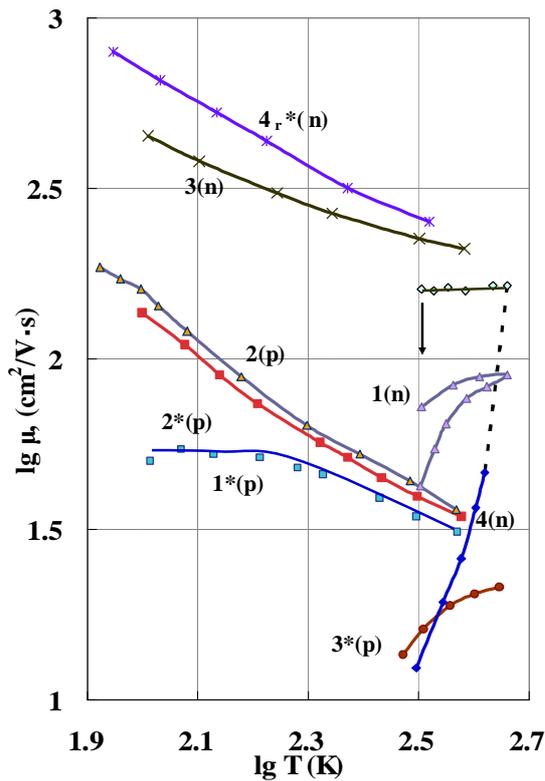
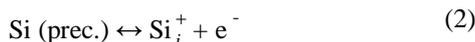
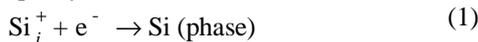


Fig. 3. Temperature dependence of the electron and hole mobility in the CdTe:Si samples (curves corresponds to the numbering in Fig. 2). The arrows on the curves 1 and 4 indicate the direction of the temperature change during the measurement.

Secondly, it is believed that Ge(Sn) impurities introduced into the lattice occupy only nodal positions Ge_{Cd} and eventually Ge_{Te} . At the same time, considering the silicon atoms' small size one must assume also interstitial positions Si_i for Si impurity besides the nodal ones (Si_{Cd} and Si_{Te}). The latter defect provides mobility of defect-dopant system by fast interstitial or dissociative diffusion.

We assume that in CdTe crystals, doped by silicon, are present, besides uncontrolled impurities, imperfections like Si_{Cd} , Si_i , cadmium vacancies V_{Cd} , associates ($Si_{Cd}V_{Cd}$), as well as both massive and/or microscopic impurity inclusions (second phase, precipitates). In this case, the reactions of the latter with the isolated impurity atoms are written below:



i.e., the phases may grow at the expense of interstitial atoms, and precipitates can both "dissolve" and "condense". Precipitates dimensions determine the temperature range where the reaction (2) occurs intensively: the smaller the precipitates are, the lower are temperatures of the "dissolution" (if the crystal is heated) or "condensation" (when cooling) processes.

Consequently, in the 1st sample group the Si impurity is virtually eliminated from the game due to the dominance of impurity phases. And such samples show a

temperature dependence of the electrical characteristics similar to those of the undoped crystal, due to uncontrolled impurities and intrinsic defects.

It is clear that at temperatures $T \sim 373\text{--}423$ K small precipitates "evaporate" or "condense". However large inclusions (Fig. 1) are also present in such samples. They decay at STT or HTM with generation of thermal donors Si_i . This donor behavior (the n-type conductivity) of CdTe:Si sample one can see in Fig. 4 in the whole range of investigated temperatures. If we assume that a complete precipitates' breakdown occurs at the HTM, then the "final" electron density (Fig. 5) can be considered as the limit of solubility of Si impurities at high temperatures: $[Si] \sim 2 \times 10^{16} \text{ cm}^{-3}$. At low temperatures the processes of precipitates' reforming, accompanied by a decrease of the electron concentration and the formation of drift barriers, occur in samples, subjected to heat treatment with precipitate decomposition.

The precipitates' role is decisive in the group 3 samples and especially in the group 2 ones. In particular, the drift barriers are formed on space charge regions that appear due to electrons depletion of the area around the precipitates when reaction (2) goes in the reverse direction. Conversely, the progress of this reaction in the forward direction provides attenuation or even disappearance of the barrier structure.

Impurity phases and precipitates are distributed

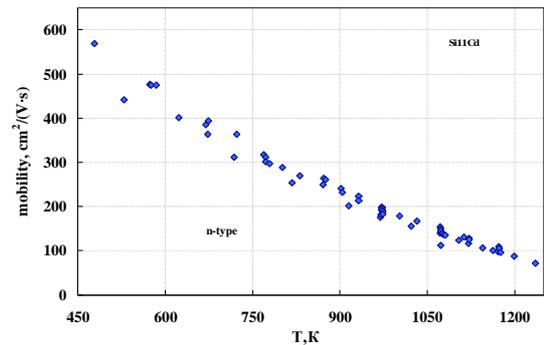


Fig. 4. The temperature dependence of the electron mobility of Group 2 sample (high-temperature measurements).

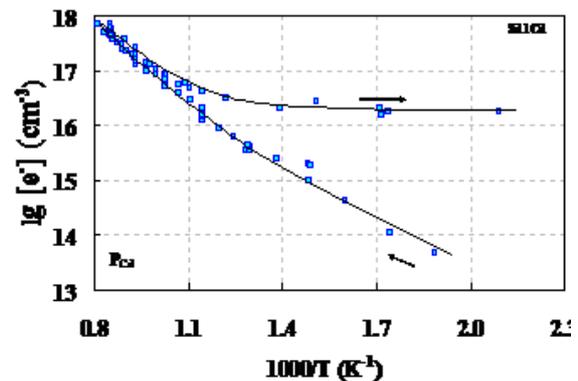


Fig. 5. The temperature dependence of the electron density of Group 2 sample (high-temperature measurements, Cd vapor pressure).

unevenly over the crystal. Therefore no position in the ingot samples ("g"-value), nor the impurity concentration in the melt (C_0), determine samples belonging to the selected group.

Samples of 2nd group show the electrical characteristics (activation energy of equilibrium conductivity, electron intrinsic photoconductivity and hole-impurity ones, thermal quenching of photoconductivity) similar to the crystal CdTe-Ge [11]. Therefore, under certain conditions, the introduction of Si impurity in CdTe crystals allows the introduction of deep acceptors (possibly, $(\text{Si}_{\text{Cd}}\text{V}_{\text{Cd}}^{2-})^-$ associates), which are slow recombination centers. However, the presence of interstitial donors Si_i in CdTe-Si crystals, and as a consequence the tendency to precipitation leads to instability of defect-dopant system unlike of stable CdTe-Ge crystals.

Conclusions

The approval of electrical inactivity of Si impurities in CdTe crystals is erroneously. This impurity provides n-conductivity of doped samples, introducing as a donor

Si_i and provides semi-insulating state by forming deep acceptor complexes $(\text{Si}_{\text{Cd}}\text{V}_{\text{Cd}}^{2-})^-$. Finally, submicron silica precipitates, that have a tend to "evaporation" at relatively low temperatures, can be seen as electrically active. Consequently, the presence of such impurities in CdTe is undesirable.

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- [1] L. Chibani, M. Hage-Ali, J. Stoguert et. al., Mater. Sci. Eng. B 16, 202 (1993).
- [2] A. Martinaitis, O. Panchuk, Sakalas A. et. al., Lithuanian Phys. Coll. (rus.) 2, 178 (1989).
- [3] F.A. Selim, V. Swaminathan, F.A. Kroger, Phys. Stat. Sol.(a). 29, 473 (1975).
- [4] O. Parfenyuk, M. Ilashchuk, K. Ulyanitsky et. al., Semiconductors 40(2), 143 (2006).
- [5] I.N. Odin, M.V. Chukichev, V.A. Ivanov, M.E. Rubina, Inorgan. Mater. 37, 445 (2001).
- [6] R. Jasinskaite, A. Martinaitis, A. Sakalas, O. Panchuk, Solid State Commun 58, 681 (1986).
- [7] R. Zelinska-Purgal, W. Nazarewicz, Phys. Stat. Sol. (b), 180, 297 (1993).
- [8] P. Fochuk, R. Grill, I. Nakonechnyi, O. Kopach, O. Panchuk, Ye. Verzhak, E. Belas, A.E. Bolotnikov, G. Yang and R. James, B.IEEE. Trans. Nucl. Sci. 58(5), 2346 (2011).
- [9] M. Sheinkman, A. Schick, Semiconductors 10(2), 209 (1976).
- [10] O. Panchuk, A. Savitskiy, P. Fochuk et. al., J. Cryst. Growth 197, 607 (1999).
- [11] Z. Zakharuk, S. Dremlyuzhenko, Kovalchuk M. et. al., Phys. Chem. Solid State 8(4), 703(2007).

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Електрична нестабільність кристалів CdTe:Si

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У роботі наведені результати досліджень температурних залежностей електропровідності та постійної Холла у кристалах CdTe, легованих кремнієм (концентрація домішки у розплаві була 10^{18} - 10^{19} см⁻³). Проведена класифікація досліджуваних зразків і умов, при яких можуть реалізуватися конкретні домішкові стани. Знайдено відмінність між трьома групами кристалів CdTe:Si: (1) - низькоомні кристалу р-типу з мілкими акцепторами, у яких домішка Si локалізована головним чином у великих вкрапленнях; (2) - напівізолюючі кристали з глибокими акцепторами і преципітатами Si субмікронного розміру, які є джерелом міжвузлових мілких донорів Si_i; (3) - низькоомні кристали, у яких n-тип провідності забезпечується мілкими донорами Si_i (і/або) Si_{Cd}. Таким чином, кремній відповідальний за n-тип провідності легованих кристалів, якщо він впроваджений як донор Si_i, і забезпечує напівізолюючий стан шляхом формування глибоких акцепторних комплексів (Si_{Cd}⁻V_{Cd}²⁻) з енергетичним рівнем (E_v + 0,65 eV). Субмікронні преципітати кремнію, що мають тенденцію до розчинення при відносно низьких температурах, можуть діяти як електрично активні центри.

Ключові слова: телурид кадмію, силіцій, легування, електричні властивості, домішка, преципітати.