

Si as dopant impurity in CdTe

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CdTe<Si> single crystals have been investigated by high-temperature Hall effect measurements under Cd vapor pressure in 200–900°C temperature range. Basing on the experimental results, the Si solubility in CdTe at 500–600°C has been supposed to be lower than $\sim 3 \cdot 10^{16}$ at/cm³. The Si segregation coefficient in CdTe is exceeds unity ($k_{segr}^* > 1$). This peculiarity of Si behavior in CdTe differs it from other IVA group elements. At high Si content in CdTe ($\sim 10^{17}$ at/cm³), it is mainly contained in precipitates. Their dissolution starts at $T \sim 500^\circ\text{C}$ and the subsequent cooling does not reduce the concentration of electrically active Si form. The dominating Si point defect is Si_{Cd}^+ , although a certain fraction of this impurity forms associates $(\text{Si}_{\text{Cd}}^+ \text{V}_{\text{Cd}}^{2-})^-$.

Монокристаллы CdTe<Si> были исследованы путем измерениями эффекта Холла под давлением пара Cd в интервале температур 200–900°C. На основании экспериментальных результатов предположено, что растворимость Si при 500–600°C меньше, чем $\sim 3 \cdot 10^{16}$ ат/см³. Коэффициент распределения Si в CdTe больше единицы ($k_{segr}^* > 1$), что отличает его от других элементов IVA подгруппы. При высоком содержании Si ($> 10^{17}$ ат/см³) большая его часть находится в преципитатах. Их растворение начинается при $\sim 500^\circ\text{C}$ и последующее охлаждение не уменьшает концентрацию электрически активной формы Si. Доминирующим точечным дефектом является Si_{Cd}^+ , хотя некоторая его часть образует ассоциаты $(\text{Si}_{\text{Cd}}^+ \text{V}_{\text{Cd}}^{2-})^-$.

Cadmium telluride is among II–VI semiconductors of good prospects that can be used to produce X-ray detectors, active elements for non-linear and IR optics, solar cells, as well as substrates for HgCdTe and CdZnTe epitaxial layers. The level of our knowledge on the structure of intrinsic and extrinsic point defects, which define the main CdTe properties, is insufficient to allow us to make use of all CdTe advantages. Silicon is one of the impurities present always in ingots grown by Bridgman techniques. It is necessary to know its influence on CdTe properties, because Si concentration ([Si]) is rather high and sometimes exceeds the content of all other impurities (in as-grown Bridgman crystals, [Si] sometimes runs up to 10^{17} at/cm³ [1, 2]). The reason is that CdTe single crystals are grown in quartz ampoules at high temperatures and the silicon atoms can migrate

from quartz into the crystal lattice. Therefore, it is very important to know the type of main existing Si point defects and their influence on CdTe properties.

Very scarce information about Si behavior in CdTe is available. The only work where the results of different investigations in CdTe<Si> crystals are presented is the paper [3]. He studied heavily-doped crystals grown by THM with Si content in the melt ([Si] = $9 \cdot 10^{18}$ at/cm³). The Si distribution along the ingot was more or less homogeneous and its concentration did not exceed 100 ppm. But the authors note a large data scatter and poor reproducibility. Cathodoluminescence (CL) study of CdTe samples has shown a strong difference of these CL spectra from as-grown or annealed in Te vapor CdTe<Si> samples [4]. In [5], a possible amphoteric behavior of Si was observed in high-temperature Hall effect measurements.

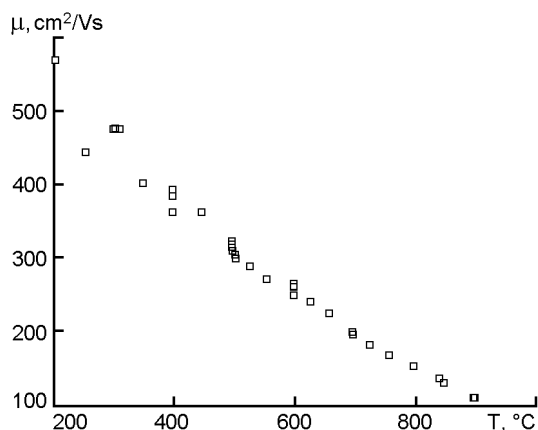


Fig. 1. Temperature dependence of electron mobility in CdTe<Si> crystals under P_{Cd} (sample Si11Cd).

These experiments were carried out under well-defined Te vapor pressure in intentionally undoped CdTe samples purified by extraction in Cd + CdTe melt [5]. IR absorption on localized modes in CdTe doped simultaneously with Li and IVA group elements (Si, Ge and Sn) has been studied in [6–7]. It was established that these elements enter the Cd sublattice producing associates. But there was found no evidence of their possibility to substitute Te atoms. Perhaps the used method was insensitive or SiTe was present in a very low concentration. The purpose of this work was to investigate electrical properties of CdTe<Si> single crystals under well-defined Cd vapor pressure (P_{Cd}) at low and high temperatures. CdTe<Si> crystals were grown by Bridgman technique from Cd, Te and Si of 6N purity. The silicon concentration in the melt was about $2 \cdot 10^{18} \text{ at}/\text{cm}^3$. The samples ($2.5 \times 2.5 \times 15 \text{ mm}^3$) were cut out from the bottom (Si11Cd sample), the middle (Si10Cd) and the top (Si9Cd) of grown ingots in order to obtain samples with various Si content. Then the samples were polished and etched. The high-temperature Hall effect measurements were carried out under well-defined P_{Cd} pressure in the 200 to 900 $^\circ\text{C}$ temperature range using direct current. The samples were placed in sealed quartz ampoules and 6 clamped graphite or welded tungsten contacts were used. It was impossible to estimate Si concentration in the samples, because its segregation coefficient (k_{segr}^*) in CdTe is unknown. But some literature sources [8] and our own experimental results allow us to suppose that its value exceeds 1. Therefore, a higher Si con-

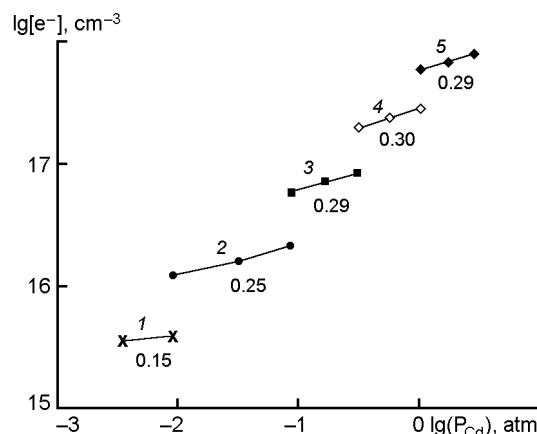


Fig. 2. Cd vapor pressure dependence of electron concentration in sample Si11Cd.

1 – 500 $^\circ\text{C}$, 2 – 600 $^\circ\text{C}$, 3 – 700 $^\circ\text{C}$, 4 – 800 $^\circ\text{C}$, 5 – 900 $^\circ\text{C}$.

tent can be expected in the CdTe ingot part crystallized first. Thus, the Si9Cd sample was expected to contain a smaller amount of that impurity than Si11Cd. So, it is the electrical properties of just those sample that can be anticipated to be influenced by Si dopant to highest extent.

At the initial stage of measurements ($T = 200\text{--}400^\circ\text{C}$), both Si9Cd and Si10Cd samples possessed the *p*-type conductivity, like the common undoped CdTe crystals. But Si11Cd demonstrated only the *n*-type conductivity from the very outset and to the very end of investigations, what is not ordinary for such crystals. The electron mobility changed from $\mu \sim 570 \text{ cm}^2/\text{Vs}$ at 200 $^\circ\text{C}$ to $\mu \sim 100 \text{ cm}^2/\text{Vs}$ at 900 $^\circ\text{C}$ (Fig. 1). The high-temperature investigation results of the Si11Cd sample are shown in Fig. 2 and 3 as Cd vapour pressure and temperature dependence of $[e^-]$, respectively. At 500 $^\circ\text{C}$, $[e^-]$ depends weakly on Cd vapour pressure (line slope $\gamma \approx 0.15$) (Fig. 2). This evidences an essential role of electrons generated by the dopant. At higher temperatures (600–900 $^\circ\text{C}$), the situation is similar to undoped CdTe under P_{Cd} . The line slopes of Cd vapor pressure dependences grow up to 1/3, what is typical in these conditions. The approximated electroneutrality equation is:

$$[e^-] = 2[\text{Cd}_i^{2+}]. \quad (1)$$

The influence of Si impurity on CdTe electrical properties is negligible.

The electrical properties of samples cut off from the ingot middle and the top were

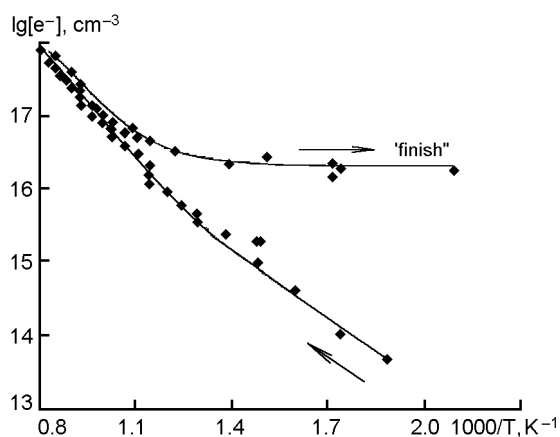


Fig. 3. Temperature dependence of $[e^-]$ for sample Si11Cd.

very close to those of undoped CdTe, too: p -type conductivity, $\mu \sim 40\text{--}50 \text{ cm}^2/\text{V}\cdot\text{s}$ and $\sigma \sim 10^{-3}\text{--}10^{-4}(\Omega\cdot\text{cm})^{-1}$ at RT. At high temperatures, their properties also did not differ from common CdTe. However, after sample heating up to 900°C , the $[e^-]$ grew more than by 2 orders (up $3\cdot 10^{16} \text{ cm}^{-3}$), which was observed in post-cooling process. The electron density stabilization at $300\text{--}500^\circ\text{C}$ is due to Si-controlled conductivity at relatively low level of intrinsic acceptor point defects (Fig. 3). An analogous effect was also observed in the Si10Cd sample: $[e^-]$ increased to $2.5\cdot 10^{16} \text{ cm}^{-3}$ after high-temperature measurements. That is why the Si solubility can be concluded to do not exceed $3\cdot 10^{16} \text{ at}/\text{cm}^3$. Such changes in $[e^-]$ after heating can be explained by Si solubility increase. Since the Si content in CdTe crystals reaches about $10^{17} \text{ at}/\text{cm}^3$, the most part of this impurity can be supposed to be located in precipitates (as the Si solubility does not exceed $3\cdot 10^{16} \text{ at}/\text{cm}^3$). At the beginning of the measurements, the concentration of electrically active Si part is about $3\cdot 10^{13} \text{ at}/\text{cm}^3$ at 250°C (Fig. 3) and heating to 400°C results in the increase of this value up to $10^{15} \text{ at}/\text{cm}^3$. The increase of magnitude by several orders is observed due to Si solubility increase caused by heating (impurity being dissolved from precipitates). The temperature dependences at constant Cd vapor pressure (Fig. 4) had the following line slopes (as determined from Arrhenius equation): 0.84 eV (1 atm.), 0.75 eV (0.1 atm.), 0.74 eV (0.01 atm.), 0.65 eV (0.001 atm.). These values are very close to those typical of the intentionally undoped CdTe.

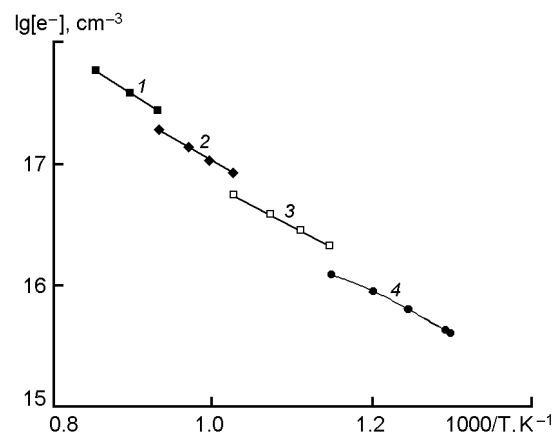
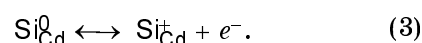
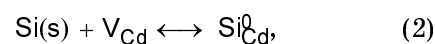
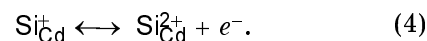


Fig. 4. Temperature dependence of electron concentration (sample Si11) under P_{Cd} : 1 atm. (1); 0.5 atm. (2); 0.1 atm. (3); 0.01 atm (4).

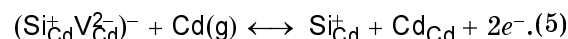
The increase of electrically active fraction of Si dopant can be described by the next equations:



The following ionization is possible at very high temperatures:



As well as the associate decay process:



But at dopant content $< 10^{17} \text{ cm}^{-3}$, the associate concentration in CdTe is low and Eq.4 does not play any essential role.

Basing on the experimental results, it is possible to assume a low Si solubility in CdTe, which does not exceed $3\cdot 10^{16} \text{ at}/\text{cm}^3$ at $500\text{--}600^\circ\text{C}$. Since the differences in electrical properties between samples with different Si content were found only in those cut out from the initial part of the ingot, the Si segregation coefficient can be supposed to exceed unity ($k_{\text{segr}}^* > 1$). This peculiarity of Si behavior in CdTe, which differs from the other IVA group elements, can be caused by the small Si atomic radius. When Si content in CdTe is high enough ($> 10^{17} \text{ at}/\text{cm}^3$), it is contained mainly in precipitates. Their dissolution begins at $T \sim 500^\circ\text{C}$ and the following cooling does not reduce the concentration of electrically active Si forms. The dominating Si point defect is Si_{Cd}^+ , although some part of

this impurity can form associates $(\text{Si}_{\text{Cd}}^+ \text{V}_{\text{Cd}}^{2-})^-$. But the achievement of sufficient self-compensation degree is hindered due to the small Si solubility in CdTe.

References

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Si як легуюча домішка у CdTe

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Монокристали CdTe<Si> досліджено вимірюваннями ефекту Холла під тиском пари Cd в інтервалі температур 200–900°C. На основі експериментальних даних припущено, що розчинність Si менша за $\sim 3 \cdot 10^{16}$ ат/см³ at 500–600°C. Коефіцієнт розподілу Si у CdTe більший за одиницю ($k_{\text{serg}}^* > 1$), що відрізняє його від інших елементів IVA підгрупи елементів. При високому вмісті Si ($\sim 10^{17}$ ат/см³) переважна його більшість знаходиться у преципітатах. Їх розчинення починається при $\sim 500^\circ\text{C}$ і наступне охолодження не зменшує концентрацію електрично активної форми Si. Домінуючим точковим дефектом є Si_{Cd}^+ , хоча деяка частина його утворює асоціати $(\text{Si}_{\text{Cd}}^+ \text{V}_{\text{Cd}}^{2-})^-$.