Hole Conductivity of Thin Layers of Cadmium Telluride with Li and Ca Impurities

1Yuriy Fedkovych Chernivtsi National University 2, Kotsybinsky Str., Chernivtsi, 58000, Ukraine
2Vasyl Stefanyk Precarpathian National University, 57, Shevchenko Str., Ivano-Frankivsk, 76018, Ukraine,
e-mail: tetyana.m.mazur@gmail.com

By low-temperature annealing of n-CdTe substrates in aqueous suspensions of LiNO$_3$ and Ca(NO$_3$)$_2$ salts $p$-conduction layers are created. The estimated concentration of free holes in diffusion layers at 300K is $(5-50)\times10^{13}\text{ cm}^{-3}$.

**Keywords**: cadmium telluride, conductivity, isovalent impurity, point defects, ionization energy.

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**I. Samples and research methods**

The base substrates were plates of $4 \times 4 \times 1\text{ mm}^3$, which were cut from a bulk CdTe crystal. In the region of room temperature, the samples had an electronic conductivity of $\sigma \approx 0.05\text{ Ohm}^{-1}\text{ cm}^{-1}$. Before doping, the plates underwent mechanical and chemical polishing in a solution of K$_2$Cr$_2$O$_7$: H$_2$O: HNO$_3$ = 4: 20: 10 and thorough washing in distilled water. As a result of these treatments, the surface of the substrates is visually perceived as a mirror, without any noticeable mechanical damage. As a result of boiling the substrates in aqueous suspensions of LiNO$_3$ and Ca(NO$_3$)$_2$, their surface layers change the electron conductivity to the hole one, which is confirmed by a change in the sign of thermoelectric force. After the end of the diffusion process, the duration of which was chosen 30 minutes, the samples were washed 3-5 times in boiling distilled water to remove residual salts. A schematic representation of the samples that have passed the boiling stage is shown in Fig. 1, with the diffusion $p$-layer being formed on all surfaces of the substrate.

Strips of gold were deposited on one of the large sides of the plate by chemical precipitation, which served as ohmic contacts to the diffusion layer. The linearity of the current-voltage characteristics (CVC) of these contacts confirms their resistance and hole-like conductivity of the layers obtained. Note that similar contacts to base substrates are nonlinear, which
indicates the presence of a potential barrier between Au and n-CdTe. The activation energies $E_a$ of the electrically active doping centers of Li and Ca layers were found from the temperature dependences of the resistance $R$ between two ohmic contacts. The temperature could be changed within 300-480 K and maintained in the process of measuring the current-voltage characteristic with an accuracy of ± 0.5 K.

II. Discussion of research results

To estimate the concentration of free holes $p_0$ and the ionization energy $E_a$ of electrically active centers, we use the well-known expression for electrical conductivity

$$\sigma_p = e^* \mu_p \cdot p_0$$

(1)

It also $\sigma_p$ depends on temperature in a complex way due to different laws of change $\mu_p(T)$ and $p_0(T)$, which according to [5] are described by expressions of the form

$$\mu_p(T) \sim T^m$$

and

$$p_0(T) \sim T^{3/2} \exp(-E_a/nkT)$$

(2)

It $m$ depends on the mechanism of scattering of carriers and varies from -3/2 to 3/2, and $n=1$ or $n=2$ either for a strongly or slightly compensated semiconductor. Let us pay attention to the fact that in experience it is much easier to measure the resistance of a layer $R_p$, the expression for which includes $\sigma_p$, namely

$$R_p = \frac{l_0}{\sigma_p \cdot S} = \frac{l_0}{\sigma_p \cdot l \cdot d}$$

(3)

Here $d$ is the thickness of the diffusion layer, $l$ is the width of the ohmic Au-contact, $l_0$ – the distance between them, fig.1. Correctness of the measurement $R_p$ is due to the fact that the diffusion $p$-layer is isolated from the low-level $n$-substrate by a high-level $i$-region, which electrically "solves" them.

The energy of ionization of electrically active centers can be found from the dependence $R_p(T)$, assuming that it is determined, mainly, by the exponential factor $p_0(T)$ for the formula (1). This is confirmed by the given rice. 2, from which it is evident that the investigated dependencies $R_p(T)$ in coordinates $\ln R_p \cdot T^0 / T$ are direct, the energy inclination of which coincides with $E_a$. Calculated energy values, taking into account the strong compensation, are 120 meV for the layers CdTe:Li and 100 meV and 175 meV for the layers CdTe:Ca respectively. To facilitate the identification of the identified centers, we will conduct a qualitative analysis of the mechanisms of defect formation for the used impurities. At the same time, it is necessary to take into account both the placement of these elements in the Mendeleev table and their atoms in the CdTe crystalline lattice. In addition, Ca is an element of the second group that plays the role of isovalent impurity (IVI) in cadmium telluride, which, unlike the usual Li-type impurity, does not always form local levels in the forbidden semiconductor zone, but can stimulate the generation of own point defects (OPD) of the donor or acceptor type [6]. In this regard, the participation of these two representatives of the 1st and 2nd groups of the Mendeleev table in the processes of defect formation of CdTe requires a more detailed consideration for each of the impurities.

Li atoms, in principle, can form two types of levels (acceptor and donor), depending on the position occupied in the crystalline lattice CdTe. While in the nodes of cationic (cadmium) subgroups, lithium forms acceptor centers with an ionization energy of ~ 70 meV [2], which is not consistent with the energy found from the dependence, curve 1 in Fig. 2. In this connection, it should be assumed that the conductive conductivity of the layers of CdTe: Li is due to the so-called A-center, which consists of negative double-charge cadmium vacancies and a small donor level formed by the interstitial lithium atom $Li_i$ [2].

In order to obtain, as a result of isovalent doping, Ca self-defects of the acceptor type (cadmium

![Fig. 1. Schematic representation of the structure of research objects.](image)

![Fig. 2. Temperature dependence of the resistance between two ohmic contacts for the layers of CdTe: Li (1) and CdTe: Ca (2).](image)
vacancies $V_{Cd}$ and interstitial tellurium $Te_i$), it is necessary that the effective charge of cadmium telluride $Q_{CdTe}^e$ is less than the effective charge of the compound, which includes VI. Assuming calcium is included in the cationic substrate nodes, the effective charge of the CaTe compound will be greater than CdTe, i.e. $Q_{CdTe}^e < Q_{CaTe}^e$. (Note that the effective charges were calculated by the Pauling formula, taking into account the electronegativity of the elements Cd, Ca and Te [6]). With the indicated inequality, VI contributes to the generation OPD of the acceptor-type that are $V_{Cd}$ and $Te_i$. However, in this case, the activation energy (curve 2 in Fig. 2) does not coincide with the ionization energies of these centers, which indicates a more complex ensemble of the created OPD. Finding out the causes of these differences, require additional research, in particular, low-temperature luminescence, which goes beyond the scope of this work.

Thus, the presented results convincingly testify to the possibility of obtaining a sufficiently high hole conductivity in CdTe by low-temperature annealing of substrates in a water suspension of LiNO$_3$ and Ca (NO$_3$)$_2$ salts. Further research should be aimed at the development of methods for determining the thickness of diffusion layers, as well as the establishment of the composition of point defects and their basic parameters.

Conclusions

In conclusion, we estimate the concentration of free holes in diffusion layers at room temperature, taking thickness $d = 10 \mu m$ for samples of both types. Taking into account the typical mobility of holes $\mu_p \approx 50 / V \cdot cm$ 50 cm$^2$/Vs [2], we obtain that in the obtained layers it is within $(5-50) \times 10^{15}$ cm$^{-3}$. This is quite high, taking into account the anomalously low (~ 400 K) doping temperature.

References

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В.П. Махній1, Т.М. Мазур2, М.М. Березовський1, О.В. Кінзерська1, В.В. Прокопів2

Діркова провідність тонких шарів кадмій телурид з домішками Li та Ca

1Чернівецький національний університет імені Юрія Федьковича, вул. Коюбінського, 2, 58000, м. Чернівці, Україна
2Прикарпатський національний університет імені Василя Стефаника, вул. Шевченка, 57, 76018, м. Івано-Франківськ, Україна, e-mail: teryana.m.mazur@gmail.com

Низькотемпературним відпалом підкладок n-CdTe у водяних суспензіях солей LiNO$_3$ та Ca(NO$_3$)$_2$ створені шари p-типу провідності. Оціночна концентрація вільних дірок в дифузійних шарах при 300 К становить $(5-50) \times 10^{15}$ см$^{-3}$.

Ключові слова: кадмій телурид, провідність, ізовалентна домішка, точкові дефекти, енергія іонізації.