DOI: 10.15330/pcss.19.4.313-315

UDK: 535.37 ISSN 1729-4428

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

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By low-temperature annealing of n-CdTe substrates in aqueous suspensions of LiNO₃ and Ca(NO₃)₂ salts p-conductivity layers are created. The estimated concentration of free holes in diffusion layers at 300K is $(5-50)\cdot 10^{15}$ cm⁻³.

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

Article acted received 16.09.2018; accepted for publication 15.12.2018.

Introduction

Despite the fact that cadmium telluride has bipolar conductivity, obtaining low-resistance crystals or *i*-layers of *p*-type layers continues to be an urgent task [1,2]. This is due to the need for *p*- *n* junctions with low series resistance, as well as the problem of creating low-resistance ohmic contacts to high-resistance *p*-CdTe. In addition, *p*-CdTe thin films are promising for creating photocells based on CdS/CdTe, ITO/CdTe heterostructures, etc. [3]. Meanwhile, despite a number of advantages of thin-film variants of devices compared to crystal ones, by now, unfortunately, there are no reproducible technologies for the synthesis of thin films CdTe on foreign substrates with the required parameters.

In view of the above, as substrates, it is more expedient to use monocrystalline cadmium telluride, whose growing methods are developed quite well [1, 2]. When choosing the method and modes of creation on such substrates of layers with hole conductivity, it is necessary to observe conditions that do not cause changes in the basic parameters of the base material. Such, in particular, may be the technology of introducing doping impurities from an aqueous suspension of its salts, which was successfully implemented by the authors [4] to obtain a hole conductivity of $\sigma \approx 1$ Ohm⁻¹ cm⁻¹ at 300 K using Ba (NO₃)₂ salt.

In this work, the described method is used for doping CdTe with other impurities, which are Li and Ca.

I. Samples and research methods

The base substrates were plates of $4 \times 4 \times 1$ mm³, which were cut from a bulk CdTe crystal. In the region of room temperature, the samples had an electronic conductivity of $\sigma \approx 0.05$ Ohm⁻¹ cm⁻¹. Before doping, the plates underwent mechanical and chemical polishing in a solution of $K_2Cr_2O_4$: H_2O : $HNO_3 = 4$: 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 LiNO₃ and Ca(NO₃)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

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

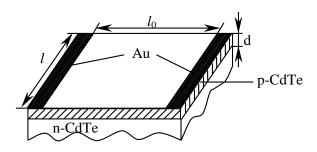


Fig. 1. Schematic representation of the structure of research objects.

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 \pm 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

$$\sigma_p = e \cdot \mu_p \cdot p_0 \tag{1}$$

It also σ_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

$$\mu_p(T) \sim T^m \text{ and } p_0 \sim T^{3/2} \exp(-E_a / nkT)$$
 (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 σ_p , namely

$$R_p = \frac{l_0}{\sigma_p \cdot S} = \frac{l_0}{\sigma_p \cdot l \cdot d} \tag{3}$$

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 $R_n(T)$ coordinates $\ln R_p - 10^3 / T$ 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 Litype 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

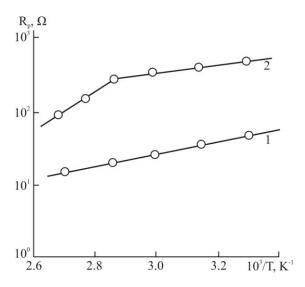


Fig. 2. Temperature dependence of the resistance between two ohmic contacts for the layers of CdTe: Li (1) and CdTe: Ca (2).

vacancies V_{Cd} and interstitial tellurium Te_i), it is necessary that the effective charge of cadmium telluride Q_{CdTe}^* is less than the effective charge of the compound, which includes IVI. Assuming calcium is included in the cationic substrate nodes, the effective charge of the CaTe compound will be greater than CdTe, i.e. $Q_{CdTe}^* < Q_{CaTe}^*$. (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, IVI 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, lowtemperature luminescence, which goes beyond the scope of this work.

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 $\mu_p \approx 50~\rm /B \cdot c$ 50 cm²/Vs [2], we obtain that in the obtained layers it is within (5-50) $10^{15}~\rm cm^{-3}$. This is quite high, taking into account the anomalously low (~400 K) doping temperature.

Conclusions

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 LiNO₃ and Ca (NO₃)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.

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Діркова провідність тонких шарів кадмій телуриду з домішками Li та Ca

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Низькотемпературним відпалом підкладок n-CdTe у водяних суспензіях солей LiNO₃ та Ca(NO₃) $_2$ створені шари р-типу провідності. Оціночна концентрація вільних дірок в дифузійних шарах при 300 К становить (5-50)· $_10^{15}$ см-3.

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