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Electrical properties of CdTe<Ca> thin layers

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The technique of obtaining thin layers of cadmium telluride of p-type conductivity by chemical doping of the surface of cadmium telluride crystals by calcium is described.

The dependences of the electrical properties of the obtained films on the technological factors of their production are investigated. The conductivity of the doped layer, velocity and depth of diffusion are determined.

Keywords: cadmium telluride, conductivity, concentration, point defects.

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Introduction

The second generation of solar cells is promising due to the use of common thin-film materials: cadmium telluride (CdTe), a mixture of copper, indium, gallium, and selenium. Typically, the thickness of the light-absorbing semiconductor layer is only 1 to 3 microns. The process of producing such photovoltaic cells is more automated and has a much lower cost

Despite the fact that cadmium telluride has bipolar conductivity, the production of low-resistance crystals or p-type layers continues to be an urgent task [1]. This is due to the need for p-n junctions with low sequential resistance, as well as the problem of making low-ohmic contacts to high-ohmic p-CdTe. In addition, p-CdTe thin films are promising for photovoltaics cell based on CdS/CdTe, ITO/CdTe heterostructures [1].

This paper describes a technique for obtaining thin layers of cadmium telluride p-type conductivity by chemical doping of the surface of calcium cadmium crystals with calcium.

The dependences of the electrical properties of the obtained films on the technological factors of their production are investigated.

I. Experimental procedure

As base substrates for obtaining the doped films were used 5×5×2 mm³ plates, which were cut from a CdTe

bulk crystal. The original components for the synthesis of ingots were taken to be 99,999 pure. The plates were mechanically and chemically polished before doping in K₂Cr₂O₄:H₂O:HNO₃ = 4:20:10 solution to obtain a mirror surface without mechanical defects and thorough washing in distilled water. Doping was carried out by boiling the substrates in aqueous suspensions of Ca(NO₃)₂. The duration of doping process varied from 15 to 60 min. At the end of the diffusion process, the samples were washed several times in boiling distilled water to remove residual salts.

Measurement of electrical parameters of semiconductor films was carried out on the developed automated device according to the classical method, when a sufficiently high voltage is applied to the sample and the current flowing through the sample is measured. During the measurement, the film samples were located in a holder of a typical structure [2] made on a fluoroplastic basis with four measuring probes and a built-in standard resistor for measuring current by a digital microvoltmeter. The holder is secured via a detachable connection in the middle of the aluminum cylinder, which has build-in the PT100 temperature sensor. The obtaining of reliable ohmic contacts, which do not break the film and satisfy all necessary requirements [2,3], was carried out by methods of deposition of silver in combination with gilded clamp contacts or by the use of silver-containing conductive

adhesives. The choice of the main contact material was determined by its output, temperature and mechanical properties. Control of the properties of the made contacts was carried out by analyzing the VAC of samples [4]. The type of conductivity was determined by the sign of thermo-emf [4].

II. Electrical model of resistance of rectangular sample

Since doping affects only the conductivity of the surface layer, a rectangular sample can be represented as a parallelepiped with height h and base $l \times l$, which has doped walls with effective thickness d (Fig. 1a). Then the linear size of the undoped crystal will be equal $h_0 = h - 2d$, $l_0 = l - 2d$ and its resistance $R_0 = \rho_0 / h_0 = \rho_0 / (h - 2d)$, where ρ_0 is the resistivity of the pure material. In addition, such an electrical cell will have four more resistivity elements of doped lateral surfaces R_{gl} , which are included in parallel and two resistivity elements in series to R_0 (Fig. 1b) [5]:

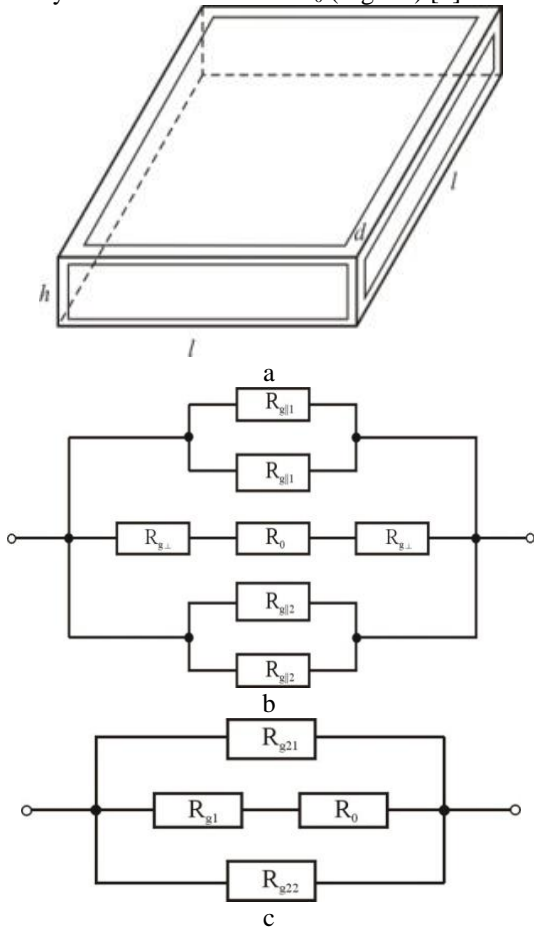


Fig. 1. Model of CdTe crystal with alloyed surface (a) and its equivalent electrical circuit (b, c).

$$R_{g21} = \frac{1}{2} R_{gl1} = \frac{\rho_g}{2d} \tag{2}$$

$$R_{g22} = \frac{1}{2} R_{gl2} = \rho_g \frac{l}{2d(h-2d)}$$

$$R_{g1} = 2R_{g\pm} = \rho_g \frac{2d}{(1-2d)(h-2d)} \tag{3}$$

Here, ρ_g is the resistivity of the doped region.

Taking into account the equivalent scheme (Fig. 1, c), the total resistance of the rectangular sample with doped regions R_e will be determined by the relation:

$$\frac{1}{R_e} = \frac{1}{R_0 + R_{g1}} + \frac{1}{R_{g21}} + \frac{1}{R_{g22}}$$

$$R = \frac{(R_0 + R_{g1})R_{g21}R_{g22}}{R_{g21}R_{g22} + (R_0 + R_{g1})R_{g22} + (R_0 + R_{g1})R_{g21}} \tag{4}$$

Knowing the resistance of the electrical cell of the film R , it is possible to determine its equivalent resistivity:

$$\rho = Rh \tag{5}$$

Considering the justified assertion that the resistivity inside the sample (ρ_0) does not change during doping of the surface, and the resistivity of the surface layer (ρ_g) depends on the concentration of the doping solution and the effective thickness on which the doping impurity penetrates and depends on in the doping solution, and having experimental data for different doping times, it is possible to determine the resistivity and thickness of the doped layer (Figs. 2 - 4, Table 1).

Table 1

Parameters calculated from the electrical model for thin CdTe:Ca layers

$R_0, \text{ Ohm}$	$3.45 \cdot 10^6$
$h, \text{ cm}$	0.2
$l, \text{ cm}$	0.5
$r, \text{ Ohm} \cdot \text{ cm}$	$6.90 \cdot 10^5$
$R_g, \text{ Ohm} \cdot \text{ cm}$	2400
$R_g, \text{ Ohm} \cdot \text{ cm}$	900
$R_g, \text{ Ohm} \cdot \text{ cm}$	600

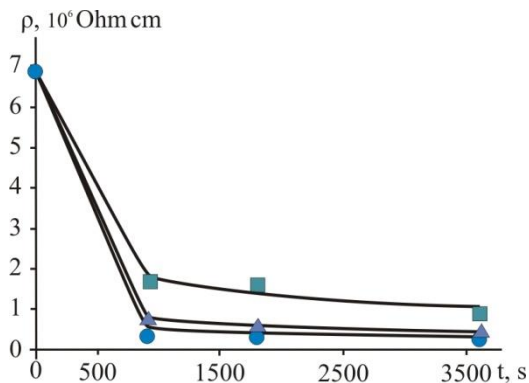


Fig. 2. Dependence of specific resistance on the time of doping (solution concentration ■–25%, ▲–50%, ●–75%).

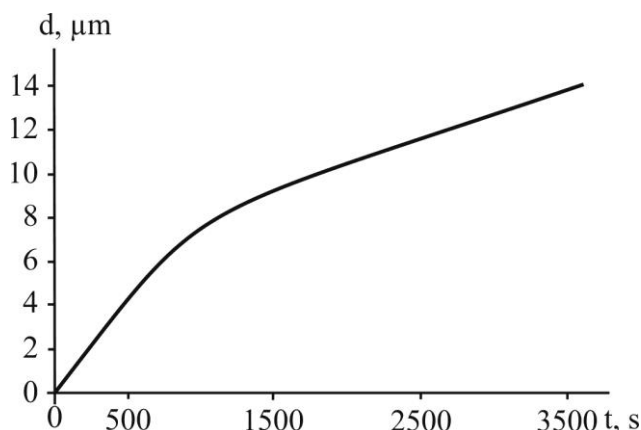


Fig. 3. Dependence of the penetration thickness of the dopant on the time of doping.

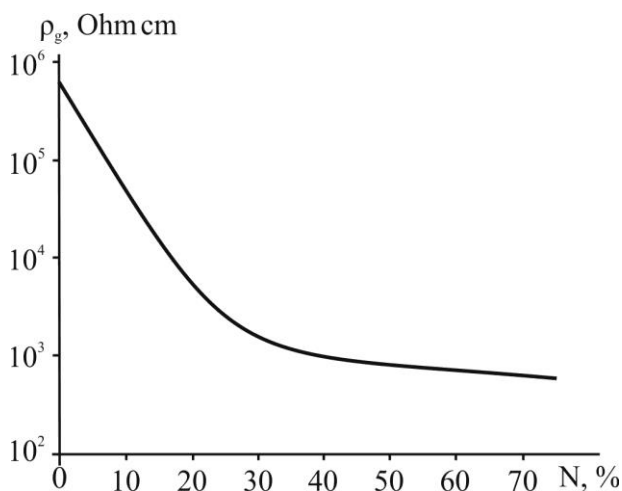


Fig. 4. The dependence of the resistivity.

III. Results and discussion

If the concentration of atoms in some near-surface layer is constant N_0 , that is, in place of the atoms that diffused deep into the sample, new ones fit (unlimited source), then the distribution of impurity by depth is determined by the equation

$$N(x,t) = N_0 \operatorname{erfc}\left(\frac{x}{\sqrt{4Dt}}\right). \quad (6)$$

Here D – ion diffusion coefficient Ca , x – coordinate, t – time of diffusion.

The concentration of Ca ions is defined as

$$N_0 = \frac{m}{M} V^{-1} N_A$$

where m – mass of substance, M – molar mass, V – volume.

Table 2

Parameters of doped thin $\text{CdTe}:\text{Ca}$ layers

	25 %	50 %	75 %
N, cm^{-3}	$1.5 \cdot 10^{20}$	$3.0 \cdot 10^{20}$	$4.5 \cdot 10^{20}$
$D, \text{cm}^2/\text{s}$	$3.00 \cdot 10^{-12}$		

It is possible to construct a thickness distribution profile for different doping times (Fig. 5).

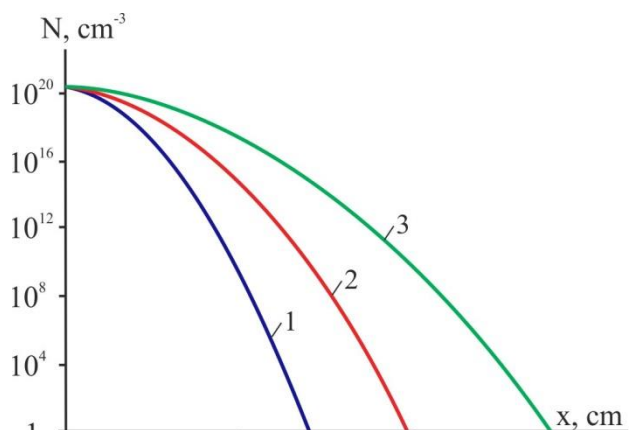


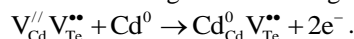
Fig. 5. The thickness distribution profile of concentration for different doping times: 1 – 15 min, 2– 30 min, 3–60 min.

Ca , being an element of group II, plays the role of an isovalent impurity in cadmium telluride, which does not always form local levels in the band gap of a semiconductor, but can stimulate the generation of own point defects of the donor or acceptor type [6].

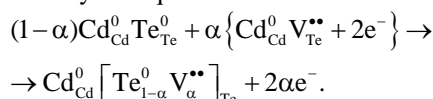
To obtain acceptor-type intrinsic defects (cadmium vacancy V_{Cd} and interstitial tellurium Te_i) as a result of isovalent Ca -doping, it is necessary that the effective charge of cadmium telluride Q_{CdTe}^* be less than the effective charge of the compound, which contains the isovalent impurities. If we assume that calcium is incorporated at the sites of the cationic sublattice, then the effective charge of CaTe will be greater than CdTe , i.e. $Q_{\text{CdTe}}^* < Q_{\text{CaTe}}^*$. (Note that the effective charges have been calculated using the Pauling formula considering the electronegativity of Cd , Ca , and Te [6]). According to the above-mentioned inequality, isovalent impurity contributes to the generation of intrinsic point defects of acceptor type, such as V_{Cd} and Te_i .

For qualitative description of defect formation in the crystal structures, it is convenient to use the method of crystalloquasichemical analysis that was successfully implemented for modelling the defect subsystem of crystals in systems based on lead telluride [7, 8]. Crystalloquasichemical approach is based on the superposition of crystalloquasichemical clusters of basic and doping compounds [9]. These clusters are formed on the basis of antistructure, which has the form of $V_{\text{Cd}}^{//}V_{\text{Te}}^{**}$ for cadmium telluride, where $V_{\text{Cd}}^{//}$ and V_{Te}^{**} are doubly charged cadmium and tellurium vacancies, respectively, “/” and “.” indicate negative and positive charges, respectively. Considering the proposed model of defect subsystem of CdTe thin films [10], appropriate crystalloquasichemical formulae are presented as following.

Crystalloquasichemical cluster of $n\text{-CdTe}$ (excess cadmium in the range of the homogeneity region):

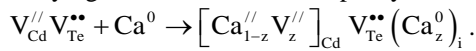


And crystalloquasichemical formula of $n\text{-CdTe}$ is



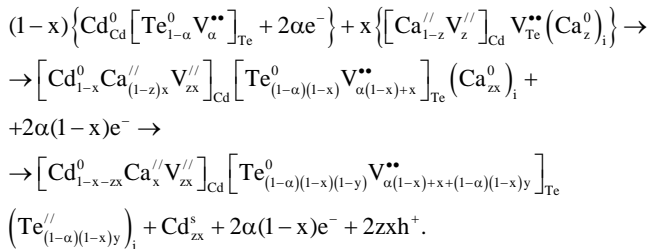
Here α is deviation from stoichiometry on the side of Cd, e^- is an electron.

Alloying cluster for calcium impurity is



Here z is the coefficient of disproportionation of calcium in CdTe lattice structure.

Superposition of the alloying cluster and the base compound n-CdTe:Ca:



Here x is calcium content, y is the coefficient of disproportionation of tellurium in CdTe lattice structure, h^+ is a hole.

Conclusion

1. The technique of obtaining thin layers of cadmium telluride p-type conductivity by chemical doping of the surface of calcium cadmium crystals by

calcium is described.

2. The dependences of the electrical properties of the obtained films on the technological factors of their production are investigated. The conductivity of the doped layer, velocity and depth of diffusion are determined.

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Електричні властивості тонких шарів CdTe <Ca>

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Описано методику отримання тонких шарів кадмій телурид р-типу провідності шляхом хімічного легування поверхні кристалів кадмій телуриду кальцієм.

Досліджено залежності електричних властивостей одержаних плівок від технологічних факторів їх отримання. Визначено провідність легованого шару, швидкість та глибину дифузії.

Ключові слова: кадмій телурид, провідність, концентрація, точкові дефекти.