Electrical Properties of Cadmium Telluride Thin Films Doped with Calcium and Lithium

Vasyl Stefanyk Precarpathian National University, Ivano-Frankivsk, Ukraine, bohdan.dzundza@pnu.edu.ua

Lviv Polytechnic National University, Lviv, Ukraine

Ivano-Frankivsk National Medical University, Ivano-Frankivsk, Ukraine

The technique for obtaining thin layers of p-type cadmium telluride by chemical doping of the surface of cadmium telluride crystals with calcium or lithium has been described. The dependences of the electrical properties of the obtained films on the technological factors of their preparation have been investigated. The conductivity of the doped layer, rate and depth of diffusion have been determined.

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

Received 28 April 2020; Accepted 15 June 2020.

Introduction

Currently, one of the most promising materials for the solar cell manufacturing is cadmium telluride [1]. Typically, the thickness of the light-absorbing semiconductor layer is only 1 to 3 microns. Therefore, obtaining cadmium telluride i-layers of p-type conductivity remains the urgent task of semiconductor material science. In this regard, it is important to search for technologies for creating thin near-surface layers with new properties on base CdTe crystals without affecting the basic parameters of the base material.

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

Ca and Li concentration profiles through the thickness of films and the dependence of resistivity of the obtained films on technological factors (the doping time and the concentration of the doping solution) have been studied.

I. Experimental Procedure

Base crystals of cadmium telluride were grown by the classical Bridgman method. They are characterized by n-type conductivity and resistivity of $\rho \approx 10^3 \, \Omega \cdot \text{cm}$. 5×5×2 mm³ plates were cut from crystals. The components with a purity of 99.999 were taken for the synthesis of ingots.

The preparation of the plates was mechanical polishing to obtain a mirror surface without mechanical defects and chemical polishing in a solution of $\text{K}_2\text{Cr}_2\text{O}_7: \text{H}_2\text{O}:\text{HNO}_3 = 4:20:10$ with thorough washing in distilled water.

Doping was carried out by boiling substrates in aqueous suspensions of $\text{Ca(NO}_3\text{)}_2$ or $\text{LiNO}_3$. The doping time varied from 15 to 60 min. After completion of the diffusion process, the samples were thoroughly washed several times in boiling distilled water to remove residual salts.

The electrical parameters of the obtained films were measured using a developed automated device by the classical method, when a sufficiently high voltage is applied to the sample and the current flowing through the sample is measured [2].

The obtaining of reliable Ohmic contacts that do not destroy the film and satisfy all the necessary requirements [3, 4] was carried out by silver deposition methods in combination with gold-plated pressure contacts or by using silver-containing conductive
V.V. Prokopiv, B.S. Dzundza, S.V. Sharyn, T.M. Mazur, L.V. Turovska, O.M. Matkivskyi

adhesives. The properties of the made contacts were controlled by analyzing the I–V curve of the samples [5, 6].

The type of conductivity was determined by the sign of the thermo-EMF [5]. The sign of the thermo-EMF changed to the opposite after treatment, which has confirmed the change in electron conductivity of the surface layers to hole conductivity.

II. Electrical model of resistance of a rectangular sample

Since doping affects only the conductivity of the surface layer, a rectangular sample can be represented as a parallelepiped of height \( h \) and base \( l \times l \), which has doped walls with an effective thickness \( d \) (Fig. 1,a). Then the linear dimensions of the undoped crystal are \( h_0 = h - 2d \), \( l_0 = l - 2d \), and its resistance is \( R_0 = \rho_0 / h_0 = \rho_0 / (h - 2d) \), where \( \rho_0 \) is the resistivity of the pure material. In addition, this electrical cell has four more resistances of the doped side surfaces \( R_{g1} \) connected in parallel and two resistances \( R_{g1} \) connected in series to \( R_0 \) (Fig. 1,b):

\[
R_{g22} = \frac{1}{2} R_{g2} = \rho_g \frac{l}{2d(h - 2d)}; \\
R_{g1} = 2R_{g1} = \rho_g \frac{2d}{(1 - 2d)(h - 2d)}. \quad (3)
\]

Here \( \rho_g \) is resistivity of the doped region.

Given the equivalent circuit (Fig. 1,c), the total resistance \( R_e \) is determined by the ratio:

\[
\frac{1}{R_e} = \frac{1}{R_0} + \frac{1}{R_{g1}} + \frac{1}{R_{g21}} + \frac{1}{R_{g22}}, \quad (4)
\]

\[
R = \frac{R_0 + R_{g1}}{R_{g21}R_{g22} + (R_0 + R_{g1})R_{g22} + (R_0 + R_{g1})R_{g21}} \quad (5)
\]

Knowing the resistance of the electrical cell of the film \( R \), we can determine its equivalent resistivity:

\[
\rho = Rh. \quad (6)
\]

It is possible to determine the resistivity and thickness of the doped layer (Figs. 2-4, Table 1) using experimental data for different doping times and taking into account the following substantiated statements: the resistivity inside the sample (\( \rho_0 \)) does not change when doping the surface, and the resistivity of the surface layer (\( \rho_g \)) depends on the concentration of the dopant, and the effective thickness penetrated by the dopant depends on the doping temperature and the exposure time in the doping solution.

Table 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_0, \ \Omega )</td>
<td>3.45 \times 10^4</td>
</tr>
<tr>
<td>( h, \ \text{cm} )</td>
<td>0.2</td>
</tr>
<tr>
<td>( l, \ \text{cm} )</td>
<td>0.5</td>
</tr>
<tr>
<td>( \rho_0, \ \Omega \cdot \text{cm} )</td>
<td>6.90 \times 10^5</td>
</tr>
<tr>
<td>( \rho_g, (\text{Ca(NO}_3)_2, 25 %) ), ( \Omega \cdot \text{cm} )</td>
<td>2400</td>
</tr>
<tr>
<td>( \rho_g, (\text{Ca(NO}_3)_2, 50 %) ), ( \Omega \cdot \text{cm} )</td>
<td>900</td>
</tr>
<tr>
<td>( \rho_g, (\text{LiNO}_3, 25 %) ), ( \Omega \cdot \text{cm} )</td>
<td>250</td>
</tr>
</tbody>
</table>

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

\[
R_{g21} = \frac{1}{2} R_{g2} = \rho_g \frac{l}{2d}; \quad (2)
\]

Fig. 2. Dependence of resistivity on doping time (solution concentration: ♦ – 25 % Ca(NO}_3)_2, ■ – 50 % Ca(NO}_3)_2, ○ – 25 % LiNO}_3). Points – experiment, solid line – calculation by electrical model.
Electrical Properties of Cadmium Telluride Thin Films Doped with Calcium and Lithium

If the concentration of atoms in a certain surface layer is a constant value \( N_0 \), that is, instead of the atoms that were diffused deep into the sample, new ones (an unlimited source) are suitable, then the depth distribution of the dopant is determined according to the equation:

\[
N(x,t) = N_0 \text{erfc} \left( \frac{x}{\sqrt{4Dt}} \right), \tag{7}
\]

Here \( D \) is diffusion coefficient of Ca or Li ions, \( x \) is coordinate, \( t \) is time.

The concentration of the doping ion is defined as

\[
N_0 = \frac{m}{M} \frac{V}{N_A}, \tag{8}
\]

here \( m \) is mass of substance, \( M \) is molar mass, \( V \) is volume.

**Table 2**

<table>
<thead>
<tr>
<th>Parameters of impurities</th>
<th>Doping solution</th>
<th>( \text{Ca(NO}_3\text{)}_2 )</th>
<th>( \text{Ca(NO}_3\text{)}_2 )</th>
<th>( \text{LiNO}_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( N_0 ), cm(^{-3} )</td>
<td>9.2·10(^{20} )</td>
<td>1.8·10(^{21} )</td>
<td>2.2·10(^{21} )</td>
<td></td>
</tr>
<tr>
<td>( D ), cm(^2)/s</td>
<td>3.00·10(^{-12} )</td>
<td>1.05·10(^{-11} )</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

It is possible to construct a concentration distribution profile over the thickness for different doping times (Fig. 4).

The diffusion coefficient calculated for Li ions turned out to be more than three times higher than for Ca ions. This can be explained by the fact that the ion radius of Li is much smaller (76 pm compared to 99 pm for Ca), and the conductivity of the n-type surface layer calculated at the same dopant concentrations and the exposure times is higher by more than an order of magnitude. All mentioned above made it possible to reduce the total resistance by 10–20 times when changing the doping with Ca to doping with Li.

The study of the current-voltage characteristic has showed the presence of a clear p-n junction between the doped surface and the undoped internal volume of the sample (Fig. 5).

**III. Crystalloquasichemical Analysis**

**Calcium doping.** Calcium, being a group II element, 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 intrinsic point defects of the donor or acceptor type [7].
If we assume that calcium is incorporated at the sites of the cationic sublattice, then the effective charge of the CaTe compound will be greater than CdTe, i.e., $Q_{\text{CaTe}} < Q_{\text{CdTe}}$. With this inequality, the isovalent impurity stimulate the generation of intrinsic acceptor-type point defects (cadmium vacancies $V_{\text{Cd}}$ and interstitial tellurium $\text{Te}_i$). Effective charges were calculated using the Pauling formula taking into account the electronegativity of the Cd, Ca, and Te elements [7].

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 telluride [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 $V''_{\text{Te}}$ 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 [10–12], crystalloquasichemical formulae are given below.

**Crystalloquasichemical cluster of n-CdTe (excess cadmium in the range of the homogeneity region):**

$$V'_{\text{Cd}}/V''_{\text{Te}} + \text{Cd}^0 \rightarrow \text{Cd}^0_{\text{Cd}}V''_{\text{Te}} + 2\text{e}^-.$$  

And crystalloquasichemical formula of n-CdTe is

$$\rightarrow \text{Cd}^0_{\text{Cd}}\left[V''_{\text{Te}}\right]_{\text{Te}} + 2\alpha \text{e}^-.$$  

Here $\alpha$ is deviation from stoichiometry on the side of Cd, $\alpha^{-}$ is an electron, “/” indicates a neutral charge.

**Alloying cluster for calcium impurity is**

$$V_{\text{Cd}}/V''_{\text{Te}} + \text{Ca}^0 \rightarrow \left[\text{Ca}^0_{\text{Cd}}V''_{\text{Te}}\right]_{\text{Cd}}V_{\text{Te}}^*\left(\text{Ca}^0_{\text{Te}}\right).$$

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

**Crystalloquasichemical formula of n-CdTe:Li as superposition of the alloying cluster and the base compound (9):**

$$\begin{align*}
(1-x)\left[\text{Cd}^0_{\text{Cd}}\left[\text{Te}^0_{\text{Te}}/\text{V}^*_{\text{a}}\right]_{\text{Te}} + 2\alpha \text{x}^{-}\right] &+ x\left[\left[\text{Ca}^0_{\text{Cd}}/V''_{\text{Te}}\right]_{\text{Cd}}V_{\text{Te}}^*\left(\text{Ca}^0_{\text{Te}}\right)\right] \\
&\rightarrow \left[\text{Cd}^0_{\text{Cd}}\text{Ca}^0_{\text{Cd}}/\text{Li}^0_{\text{Li}}\right]_{\text{Cd}}\left[\text{V}''_{\text{Te}}/\text{V}^*_{\text{a}}\right]_{\text{Te}}\left(\text{Li}^*_{\text{Li}}\right) + (1-2\alpha) \text{x}^{+}.
\end{align*}$$

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

**Lithium doping.** When studying the interaction of point defects and lithium diffusion mechanisms in CdTe crystals, the authors of [13–16] considered the possibility of the formation of interstitial lithium $\text{Li}_i$, which is a shallow donor, apart from substitutional defects $\text{Li}_{\text{Cd}}$, which act as shallow acceptors.

The acceptor effect of lithium when doping cadmium telluride, provided cadmium substitution, can be explained as follows. In CdTe crystal lattice, cadmium and tellurium ions are doubly charged $\text{Cd}^{2-}$ and $\text{Te}^{2-}$. This is due to the fact that cadmium atoms with the configuration of the valence electrons Cd (5s25p6) give two electrons to the chemical bond, i.e.

$\text{Cd}(5s^25p^6) \rightarrow \text{Cd}^{2+} (5s^25p^4)$, and tellurium atoms accept them: $\text{Te}(5s^25p^6) \rightarrow \text{Te}^{2-} (5s^25p^6)$. The formation of vacancies in the cationic sublattice or the substitution of cadmium by a monovalent impurity (for example, Li) leads to a change in both the charge and the nature of the bond with the neighboring Te atom. In this case, lithium atoms Li give one electron each when they substitute Cd and compensate for only one hole, therefore they act as acceptors: $\text{Li}^0 (2s^-)\rightarrow\text{Li}^+(2s^0)$.

Alloying cluster for lithium impurity is

$$V_{\text{Cd}}/V''_{\text{Te}} + \text{Li}^0 \rightarrow \left[\text{Li}^0_{\text{Li}}/\text{V}''_{\text{Te}}\right]_{\text{Cd}}\left[\text{V}''_{\text{Te}}/\text{V}^*_{\text{a}}\right]_{\text{Te}}\left(\text{Li}^*_{\text{Li}}\right) + (1-2\alpha) \text{x}^+.$$  

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

Crystalloquasichemical formula of n-CdTe:Li as superposition of the alloying cluster and the base compound (9):

$$\begin{align*}
(1-x)\left[\text{Cd}^0_{\text{Cd}}\left[\text{Te}^0_{\text{Te}}/\text{V}^*_{\text{a}}\right]_{\text{Te}} + 2\alpha \text{x}^{-}\right] &+ x\left[\left[\text{Li}^0_{\text{Li}}/\text{V}''_{\text{Te}}\right]_{\text{Cd}}\left[\text{V}''_{\text{Te}}/\text{V}^*_{\text{a}}\right]_{\text{Te}}\left(\text{Li}^*_{\text{Li}}\right)\right] + (1-2\alpha) \text{x}^+ \\
&\rightarrow \left[\text{Cd}^0_{\text{Cd}}\text{Li}^0_{\text{Li}}/\text{Li}^0_{\text{Li}}\right]_{\text{Cd}}\left[\text{V}''_{\text{Te}}/\text{V}^*_{\text{a}}\right]_{\text{Te}}\left(\text{Li}^*_{\text{Li}}\right) + \left(1+2\alpha\right) \text{x}^{+}.
\end{align*}$$

Here $x$ is lithium content.

**Conclusion**

1. The technique for obtaining thin layers of p-type cadmium telluride by chemical doping of the surface of cadmium telluride crystals with calcium or lithium has been described.
2. The dependences of the electrical properties of the obtained films on the technological factors of their preparation have been investigated. The conductivity of the doped layer, rate and depth of diffusion have been determined. It has been shown that changing the doping with Ca to doping with Li reduces the total resistance by 10–20 times.

3. Crystalloquasichecmical models of defect formation for n-CdTe:Ca and n-CdTe:Li, which qualitatively describe the acceptor action of impurities, have been proposed. The mechanism of the generation of acceptor type intrinsic point defects V$_{\text{Ca}}$ and Te, when doping with calcium isovalent impurity has been explained. It has been shown that in the case of n-CdTe:Li, the mechanism of substitution of cationic sites by lithium is dominant.
В.В. Прокопів, Б.С. Дзундза, С.В. Шарин, Т.М. Мазур, Л.В. Туровська, О.М. Матківський

Електричні властивості тонких плівок кадмій телуриду, легованих кальцієм та літієм

Описано методику отримання тонких шарів кадмій телуриду p-типу провідності шляхом хімічного легування поверхні кристалів кадмій телуриду кальцієм або літієм. 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, кальцій, літій.