Solid state doping of Cd$_x$Hg$_{1-x}$Te epitaxial layers with elements of V group


1I. Franko Lviv National University, 1, Universitetska str., 79000 Lviv, Ukraine
2Institute for Applied Problems of Mechanics and Mathematics, NAS of Ukraine
3b, Naukova str., 79601 Lviv, Ukraine
3Yu. Fed’kovich Chernivtsi National University, 19, Universitetska str., 58012 Chernivtsi, Ukraine
4Institute of Physics of Polish Academy of Sciences, 32/46 Al. Lotnikow, 02-668 Warsaw, Poland
5Institute of Metallurgy and Materials Science, Polish Academy of Science
25 Reymonta Str., 30-059 Krakow, Poland

Abstract. Presented here are the results of studying the controlled doping with elements of V group of the periodic table, arsenic As and antimony Sb, of narrow gap Cd$_x$Hg$_{1-x}$Te epitaxial layers during the isothermal growth from the vapour phase by the evaporation-condensation-diffusion method. Three types of impurity sources have been used for solid state doping: homogeneously doped with As(Sb) single crystal substrates of CdTe, As doped buffer Cd$_y$Hg$_{1-y}$Te ($y > x$) epitaxial layers obtained by RF sputtering in mercury glow discharge onto undoped CdTe substrates, and As(Sb) implanted undoped CdTe substrates. The results of comparative analysis of galvano-magnetic measurements and SIMS spectra indicated very high, practically nearly ~100 %, electrical activity of dopants in the Cd$_x$Hg$_{1-x}$Te epitaxially grown layers.

Keywords: X-ray spectrometry, substrate, epitaxial layer.

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1. Introduction

The narrow-gap solid solutions of cadmium and mercury tellurides – Cd$_x$Hg$_{1-x}$Te ($x = 0.18...0.3$) are the most suitable semiconductor materials for producing high efficient detectors of infra-red radiation (IR) for 3 to 5 and 8 to 14 µm atmospheric windows [1]. In spite of the technological difficulties, high production cost and development of investigation of alternative materials, there exists the necessity to improve the methods of obtaining both Cd$_x$Hg$_{1-x}$Te itself and detectors based on it. When producing the photovoltaic detectors on the basis of Cd$_x$Hg$_{1-x}$Te epitaxial heterostructures, great efforts are being directed on obtaining a doped material with required electrophysical properties. The element of V group As is considered to be the most attractive acceptor impurity in Cd$_x$Hg$_{1-x}$Te, since 100 % activation of acceptor states in the material may be reached at the concentration of $5 \times 10^{18}$ cm$^{-3}$. Nevertheless, such activation levels have been achieved at liquid-phase epitaxy from melts enriched with Hg. The doped epitaxial layers of Cd$_x$Hg$_{1-x}$Te obtained by molecular-beam epitaxy possess a $n$-type of conductivity after the growth, and to achieve high-level activation of the acceptor impurity, an additional annealing in Hg vapour is used [2]. Therefore, understanding of an amphoteric nature of the impurity and possibility to control the process of impurity incorporation in Cd$_x$Hg$_{1-x}$Te are necessary for obtaining the material suitable to produce high-quality photovoltaic structures.

The aim of this paper was to investigate the processes of autodoping with the acceptor impurity As (Sb) of Cd$_x$Hg$_{1-x}$Te epitaxial layers at isothermal vapour phase growth by the method of evaporation-condensation-diffusion (ECD).

2. Experimental techniques

During the EVC epitaxial growth of Cd$_x$Hg$_{1-x}$Te layers, we used the substrates with three types of impurity sources:

I. Homogeneously doped single crystals of CdTe grown by the Bridgmann method with impurity incorporated during the synthesis process at the concentration level of $N_{As} = 10^{16}...10^{17}$ cm$^{-3}$ ($N_{Sb} = 10^{17}...10^{18}$ cm$^{-3}$).

II. Undoped CdTe (111) and CdTe (110) crystals on surfaces of which heavily doped with As ($N_{As} = 10^{19}...10^{20}$ cm$^{-3}$) epitaxial buffer films of Cd$_x$Hg$_{1-x}$Te were deposited.
III. Undoped CdTe (111) and CdTe (110) crystals on surfaces of which controlled amount of As (Sb) was incorporated by ion implantation.

The surface sources of dopant of II type were produced by RF (f = 13.56 MHz) sputtering in mercury glow discharge of wider gap (y > x) Cd$_{x}$Hg$_{1-x}$Te epitaxial buffer films (y denotes the composition of a solid solution film with a dopant, whereas x denotes the composition at the surface of Cd$_{x}$Hg$_{1-x}$Te graded-gap epitaxial layers). To introduce As with concentrations greater than 1 at.%, the sputtering of the pure element along with the target material was carried out. For obtaining the concentration less than 0.01 at.% the impurity was introduced during the target synthesis using the weight of As. The contents of impurity in the film were controlled by the area from which the sputtering took place. When using the source of III type As(Sb) impurity was implanted with the equal ion energy E = 100 keV. Homogeneity of the dopant dose did not exceed 1 %, reproducibility was 98 %.

For implementation of the vapour-phase epitaxy [3], we used silica ampoules and accessory. Flatness and mirror-like surfaces of CdTe substrates were achieved by means of an abrasive-free chemico-mechanical polishing in a bromine-butanol etchant. The mounted ampoules were evacuated by oil-free pumping down to a residual pressure of ~10$^{-4}$ Pa, afterwards they were sealed and weighted in a two-zone furnace with resistive heating. In all experiments the temperature of growth zone amounted to 600 °C. The temperature of the other zone was maintained at the level that provided the pressure of the saturated mercury vapour during the epitaxial growth equal to $P_{Hg} = (2...4)\times10^5$ Pa. In order to increase the number of mercury vacancies created at the final stage of Cd$_{x}$Hg$_{1-x}$Te epitaxy, an annealing in the isothermal regime in mercury vapour at the temperature 320 °C was carried out for 60 hours. At these regimes of growth and post-growth annealing undoped epitaxial layers of Cd$_{x}$Hg$_{1-x}$Te had n-type of conductivity.

Diagnostics of the structural changes in the near-surface regions of single crystals and epitaxial layers of Cd$_{x}$Hg$_{1-x}$Te was performed using the X-ray methods since they are non-destructive and highly sensitive to various types of distortions of atomic planes. For the research, the Berg-Barrett method in asymmetric and skew-symmetric geometry of backward diffraction was used [4, 5]. For obtaining the rocking curves (RC), we used the method of two-crystal spectrometer in a dispersionless scheme (n−n). The skew-asymmetric scheme of X-ray diffraction makes it possible to investigate selectively and layer-by-layer with a step of ~0.05 μm and less the structural changes in the near-surface layers after the influence of different external factors, for example, ion implantation. By azimuth rotation of a crystal around the diffraction vector by the angle ψ, one can realize the case when the penetration depth of X-rays would be of the same order as the depth of the disturbed by ions near-surface layers

$$L_{ext} = \frac{\lambda}{|\chi_h|}\sqrt{\gamma_0\gamma_h},$$

(1)

where

$$\gamma_{0,h} = -\cos \theta \cos \phi \sin \psi \pm \sin \theta \cos \psi,$$

(2)

$$\gamma_{0,h} = \sin \phi_h \psi,$$

(3)

where $\phi_h \psi$ are the incidence and exit angles of X-rays, θ is the diffraction angle, ψ is the disorientation angle between the planes of incidence and reflection, $L_{ext}$ is the extinction length, $\chi_h$ are the coefficients of Fourier-polarization, $\lambda$ is the wavelength, the sign "plus" corresponds to the incident and "minus" – to the diffracted ray.

Table shows the galvanomagnetic properties of Cd$_{x}$Hg$_{1-x}$Te samples investigated by the standard technique of Hall measurements at $T = 77...300$ K and the magnetic fields ranging from 0.005 to 1.7 T. The composition of Cd$_{x}$Hg$_{1-x}$Te epitaxial layers was controlled using the spectra of optical absorption. The distribution of impurity concentration and the profiles of composition of Cd$_{x}$Hg$_{1-x}$Te epitaxial layers was determined by the Secondary Ion Mass-Spectroscopy (SIMS) at Cameca IMS-6F device. Simultaneously the analysis of the impurity and the main component isotopes of Cd$_{x}$Hg$_{1-x}$Te (203Hg$^{197}$Te or 205Hg$^{195}$Cs) has been carried out. The sensitivity limit of the device for the analyzed impurities was in the range from 5×10$^{14}$ to 10$^{15}$ cm$^{-3}$.

The quantitative composition of the main components along the thickness of the grown epitaxial Cd$_{x}$Hg$_{1-x}$Te layer was determined from X-ray microanalysis spectra. Measurements of the spectra were performed on the sample cross cleavages by means of a Scanning Electron Microscope based on microanalyser JXA-50A (JEOL). The composition measurement error did not exceed 1%.

3. Results of researches

The Cd$_{x}$Hg$_{1-x}$Te epitaxial layers grown on the As homogeneously doped substrates of CdTe had the hole type of conductivity. The boundary of maximum penetration of Hg in the CdTe substrate is clearly seen in the SEM-microphotography of the cross cleavage of typical sample 73-2 grown on the CdTe substrate with $N_{As} \sim 10^{16}$ cm$^{-3}$ (Fig. 1a). The composition-distribution curve measured with the help of X-ray microanalysis for the As doped epitaxial layer (Fig. 1a) does not differ from the typical composition profiles in Cd$_{x}$Hg$_{1-x}$Te samples obtained during the epitaxy on undoped CdTe substrates with the analogous growth regimes. Fig. 1a also shows the SIMS distribution along the depth of Cd$_{x}$Hg$_{1-x}$Te epitaxial layer. The acceptor concentration determined in this sample by means of galvanomagnetic

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Table. Results of electrophysical investigation of doped with As (Sb) ECD epitaxial layers of Cd$_x$Hg$_{1-x}$Te.

<table>
<thead>
<tr>
<th>No</th>
<th>Sample number</th>
<th>Dopant source</th>
<th>$d_1$, μm</th>
<th>$x$</th>
<th>$d_2$, μm</th>
<th>$\rho_H$, cm$^2$/Q</th>
<th>$N_d$–$N_o$, cm$^{-3}$</th>
<th>$77$ K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>V-23</td>
<td>Undoped</td>
<td>0.23</td>
<td></td>
<td>64</td>
<td>7740</td>
<td>20050</td>
<td>–1480</td>
</tr>
<tr>
<td>2</td>
<td>73-2</td>
<td>Substrate</td>
<td>0.213</td>
<td></td>
<td>57</td>
<td>3741</td>
<td>150</td>
<td>–610</td>
</tr>
<tr>
<td>3</td>
<td>770-V32</td>
<td>Buffer film</td>
<td>–</td>
<td>59</td>
<td>52</td>
<td>+16</td>
<td>+37</td>
<td>1.35·10$^{15}$</td>
</tr>
<tr>
<td>4</td>
<td>771-V33</td>
<td>Buffer film</td>
<td>–</td>
<td>62</td>
<td>43</td>
<td>–91</td>
<td>+56</td>
<td>1.12·10$^{17}$</td>
</tr>
<tr>
<td>5</td>
<td>77-2(110)</td>
<td>Implanted impurity</td>
<td>0.241</td>
<td></td>
<td>67</td>
<td>5950</td>
<td>329</td>
<td>–355</td>
</tr>
<tr>
<td>6</td>
<td>80-5(Sb)</td>
<td>Substrate</td>
<td>0.19</td>
<td></td>
<td>70</td>
<td>10370</td>
<td>245</td>
<td>–200</td>
</tr>
<tr>
<td>7</td>
<td>80-6(Sb)</td>
<td>Substrate</td>
<td>0.24</td>
<td></td>
<td>80</td>
<td>11780</td>
<td>387</td>
<td>–268</td>
</tr>
</tbody>
</table>

measurements (Fig. 1b) corresponds to the real As concentration in the epitaxial layer and signifies the high (close to 100%) level of the electrical activity of the impurity.

The successful use of the above described CdTe substrates for obtaining Cd$_x$Hg$_{1-x}$Te epitaxial layers incites the search of the alternative methods of the dopant source production. Figs 2a and 2b schematically show the structures with the impurity sources which are formed on the surface of undoped CdTe single crystals used as substrates for ECD epitaxy. Below, the results of the fulfilled investigation using such sources are presented.

When doping the Cd$_x$Hg$_{1-x}$Te ECD epitaxial layers by using the structures shown in Fig. 2a, the identical technological regimes for deposition of As highly doped films in samples 770 and 771 have been used. CdTe undoped single crystals with the (111) and (110) surface orientations were used.

The film thickness of the sample 770 was 6.5 μm and the estimated impurity concentration by the target doping level was estimated to be $N_{As} \approx 10^{19}$ cm$^{-3}$, and for the sample 771 – 5 μm and $N_{As} \approx 10^{20}$ cm$^{-3}$, correspondingly.

These heterostructures were applied for As doping of the Cd$_x$Hg$_{1-x}$Te ECD epitaxial layers – samples 770-V32 and 771-V33 (Table). The initial position of the impurity source in the buffer film is shown by rectangles on the corresponding SIMS profiles (Fig. 3): the base corresponds to the film thickness, the height – to the impurity concentration in the target. After the completion of the epitaxy process in the sample 770-V32 (Fig. 3a), total smoothing of the As profile along the structure thickness has occurred, whereas in the sample 771-V33 (Fig. 3b) the source did not completely exhaust itself. The maximum residual concentration of As in the buffer film of the sample 771-V33 corresponds to the calculated concentration of dopants in the target. This is a confirmation of the effective incorporation of the impurity into Cd$_x$Hg$_{1-x}$Te films during the low temperature epitaxy in Hg glow discharge and, respectively, ensures the high efficiency of As doping for Cd$_x$Hg$_{1-x}$Te layers when used during ECD epitaxy [6].

![SEM microphotography of the cross cleavage of sample 73-2 with the profile of composition distribution and SIMS distribution of As along the depth of Cd$_{0.21}$Hg$_{0.79}$Te epitaxial layer](image1.png)
![Magnetofield dependences of the Hall coefficient and conductivity for the sample 73-2](image2.png)
Fig. 2. Structure of substrates with surface impurity sources used at doping of \( \text{Cd}_x\text{Hg}_{1-x}\text{Te} \) epitaxial layers. Impurity source on CdTe undoped single crystal substrates: a) highly doped with the As wider gap \((y > x)\) \(\text{Cd}_y\text{Hg}_{1-y}\text{Te} \) epitaxial film; b) surface layer of a substrate implanted with As (Sb) ions.

When using the As(Sb) ion implanted impurity source, the structures based on CdTe (Fig. 2b) were mounted immediately after the ion implantation without any additional chemical processing in silica ampoules and were loaded into furnaces for carrying out the ECD epitaxy process [7]. The grown layers had mirror-like surfaces.

At the initial stages of the epitaxial growth, the state of a substrate crystal structure is of paramount importance. For establishing the influence of the disturbed surface layer on the ECD epitaxy, we have carried out X-ray study of both CdTe substrates after ion implantation and \( \text{Cd}_x\text{Hg}_{1-x}\text{Te} \) doped epitaxial layers grown on them [8].

During the implantation of As ions, in the near surface regions of CdTe single crystal, the disorder and damages consisting of considerable concentration of intrinsic defects in two sublattices, cluster formations, as well as surface dislocations and stacking faults originate [9]. The set of these imperfections causes the creation of strained regions in the surface layers of a crystal, which is correspondingly reflected in the X-ray topograms and swing curves. Fig. 4 shows the most typical topograms of the CdTe single crystal surface obtained in the asymmetric (Fig. 4a) and skew-asymmetric (Fig. 4b) diffraction schemes. A peculiarity of the studied sample lies in the fact that in CdTe substrate prepared by the standard procedure As ions are implanted only into the half of its surface. In the implanted part (A) of the crystal, in contrast to the non-implanted one (B), there takes place a distortion and tailing (331) of the reflexes of the \( \text{Cu}_{K_{α1,2}} \) line doublet. The reason for this is both the bulk disturbances of crystal perfection – the availability of the fragment structure or low-angle boundaries (Fig. 4a) and the gradient of the lattice parameter in certain crystallographic directions on the crystal surface.

At azimuth rotation of a crystal around the diffraction vector, the tailings and mergings of the diffraction maxima are observed in the topograms. During the penetration of X-rays at the depth \( L_{\text{ext}} \sim 0.35 \, \mu\text{m} \), the part of the crystal no longer diffracts X-rays (Fig. 4b). Such a picture is caused by the great disorder of the crystal lattice in the subsurface layers at the depth up to 0.35 \( \mu\text{m} \) and gives rise to the strains at the interface between surface layer and implant on one side and CdTe crystal on the other.

The swing curves obtained from the As implanted crystal parts (Fig. 5a) are characterized by an increase in the curve shape asymmetry and the magnitudes of its half-width (approximately by 2 to 2.5 times). The small decay in amplitude oscillations is observed near the main maximum of the intensity. This is mainly caused by the presence of the gradient of lattice distance along the crystal normal in the implanted region. Such gradient changes in the lattice parameter amount up to \( 1.1 \times 10^{-4} \ldots 2.3 \times 10^{-7} \, \text{Å} \).

Fig. 3. SIMS distribution of the As concentration and \( ^{202}\text{Hg}^{133}\text{Cs} \) signal along the thickness of \( \text{Cd}_x\text{Hg}_{1-x}\text{Te} \) ECD epitaxial layers grown on undoped epitaxial buffer films of \( \text{Cd}_y\text{Hg}_{1-y}\text{Te} \). For the sample 770-V32: \( N_{\text{As}} \sim 10^{19} \, \text{cm}^{-3} \), CdTe (111) (a), 771-V33: \( N_{\text{As}} \sim 10^{20} \, \text{cm}^{-3} \), CdTe (110) (b).
Fig. 5. Rocking curves of diffraction reflection of CdTe single crystal. CuK$_\alpha$-radiation, symmetric scheme of diffraction, (111) incidence, (333) reflection (a). Profiles of deformation and impurity distribution in the near surface region of CdTe (111) crystal after As implantation (b).

It follows from the analysis of X-ray structural data (Fig. 7) that the grown layers are perfect – in the topograms (Fig. 7a) a clear separation of the K$_\alpha$-doublet lines is seen. At the same time, there are local regions that do not diffract X-rays, with a density of $\approx 10^3$ cm$^{-2}$ and dimensions of 50–100 $\mu$m, among them tellurium inclusions are possible. The RC intensity distribution shown in Fig. 7b has a characteristic Gaussian form. The half-width of the rocking curves for the sample 77-2 is in the range of 70'' to 80''. This is indicative of the fact that annihilation of radiation defects and recrystallization of the disordered near surface layers in CdTe substrate occur at the initial stages of ECD epitaxy and do not result in deterioration of the crystal structure in Cd$_{0.22}$Hg$_{0.78}$Te doped epitaxial layers.

The high efficiency of doping from the As solid state source during the ECD epitaxial growth [7] has given an incitement to use another element of V group, Sb, as an impurity. Its successful usage for the liquid phase epitaxial layers of Cd$_{0.22}$Hg$_{0.78}$Te has been shown by the
authors of the paper [13]. The choice of antimony is caused by the following reason. Impurities of V group (P, As) in CdTe crystals are shallow acceptors [14]. This provides comparatively high conductivity of this material, and Sb doping provides the possibility of obtaining semisolating material where the conductivity is controlled by deep acceptors with energy separated levels [15]. The latter is attractive from the viewpoint of improving the electrophysical properties of Cd_{x}Hg_{1-x}Te epitaxial layers. This takes place due to the reduction of the influence of transition regions epitaxial layer – substrate on these properties.

We used the homogeneously Sb doped CdTe single crystals \( (N_{\text{Sb}} \approx 10^{17} \text{ cm}^{-3}) \) and the structures shown in Fig. 2b as substrates for epitaxial growth of Cd_{x}Hg_{1-x}Te by the ECD method. Table lists the resulting electrophysical properties of the Cd_{x}Hg_{1-x}Te ECD epitaxial layers of samples 80-5 and 80-6. In both cases, we can observe that, during the epitaxy, similarly to As doping, there occurs uniform doping of the grown graded-gap layer of Cd_{x}Hg_{1-x}Te with Sb, and the carrier concentration correlates with the Sb concentration determined by the SIMS technique.

Fig. 6. SIMS distribution of As and \(^{202}\text{Hg}^{133}\text{Cs}\) signal along the thickness of Cd_{x}Hg_{1-x}Te ECD epitaxial layer of the sample 77-2 (a); magnetofield dependences of the Hall coefficient and conductivity (b).

Fig. 7. Topogram of the sample 77-2. CuK\(_\alpha\)-radiation, (111) surface of incidence: symmetric scheme of diffraction, (333) reflection, \( \times 18, L_{\text{ext}} = 7.6 \mu\text{m} \) (a); rocking curve of the sample 77-2 (b).

Fig. 8. SEM microphotograph of cross cleavage of the sample 92-4 with the profile of composition distribution and SIMS distribution of Sb along the thickness of Cd_{x}Hg_{1-x}Te epitaxial layer (a); topogram of the sample 92-4: CuK\(_\alpha\)-radiation, skew-asymmetric scheme of diffraction: (111) plane of incidence, (511) reflection – \( \varphi = 90^\circ, \Phi_0 = 29^\circ, L_{\text{ext}} = 1.01 \mu\text{m} \) (b).
For example, Fig. 8a illustrates the typical SEM microphotography of the cross cleavage with the shown distribution profiles of both the impurity and composition measured using the X-ray microanalyser for the sample 92-4, where the implanted with Sb undoped CdTe surface was used as a dopant source \( E = 100 \text{ keV}, \ D = 8 \times 10^{14} \text{ cm}^{-2} \).

For the study of the quality of the grown epitaxial layers, we have carried out X-ray topographical investigation. Fig. 8b shows the topogram of the sample 92-4 where the lines of \( K_{\alpha} \)-series are separated without broadening and distortion. This allows one to conclude that grown Cd\(_{x}\)Hg\(_{1-x}\)Te epitaxial layers doped with Sb are uniform and structurally perfect.

4. Conclusions

Cd\(_{x}\)Hg\(_{1-x}\)Te epitaxial layers with close to 100 % level of electrical activity of the impurities have been obtained using doping with arsenic (antimony) during isothermal vapour phase epitaxy.

Investigation of the peculiarities of ion implantation of the epitaxial layers allows to obtain information concerning the behaviour of physical processes and establish the mechanisms responsible for changes in the defect sub-system of Cd\(_{x}\)Hg\(_{1-x}\)Te epitaxial layers.

The structural defects in disordered regions of radiation damages, which are created during the As (Sb) implantation with an energy of 100 keV in the near surface layers of CdTe single crystal substrates at irradiation doses of \( D < 5 \times 10^{15} \text{ cm}^{-2} \), annihilate at the initial stages of epitaxy and virtually do not influence the structural perfection of the grown Cd\(_{x}\)Hg\(_{1-x}\)Te epitaxial layers.

References

3. V.G. Savitsky, O.P. Storchun, Preparation of Hg\(_{1-x}\)CdTe \( 0.1 < x < 0.5 \) epitaxial layers by two-stage evaporation-condensation-diffusion method // Thin Solid Films 317, p. 105-107 (1998).