Conductivity type conversion in p-Cd$_x$Hg$_{1-x}$Te

N.N. BERCHENKO$^1$, V.V. BOGOBOYASHCHYY$^2$, I.I. IZHNIN$^3$, K.R. KURBANOV$^4$, A.P. VLASOV$^5$, and V.A. YUDENKOV$^3$

$^1$Institute of Physics, Rzeszow University, 16A Rejtana Str., 35-310 Rzeszow, Poland
$^2$Kremenchug State Polytechnical University, 20 Pershotravneva Str., 39614 Kremenchug, Ukraine
$^3$R&D Institute for Materials SRC “Carat”, 202 Stryjska Str., 79031 Lviv, Ukraine
$^4$Institute of Economy and New Technologies, 24/37 Proletarskaya Str., 39614 Kremenchug, Ukraine
$^5$Lviv National University, 49 Chuprynky Str., 79046 Lviv, Ukraine

Investigations and comparative analysis of p-to-n type conductivity conversion processes on the identical samples of vacancy doped p-Cd$_x$Hg$_{1-x}$Te (x = 0.2) under ion-beam milling (IBM) and anodic oxide annealing and on the identical samples of As-doped p-Cd$_x$Hg$_{1-x}$Te (x = 0.22) under IBM and anodic oxide annealing have been carried out. The conductivity type conversion has been observed at the considerable depth of the vacancy doped material both under IBM or under anodic oxide annealing while in the case with As-doped material only under IBM. It was considered that conversion in all these processes was determined by the mercury interstitial diffusion from corresponding mercury diffusion source and recombination with its native acceptors – cationic vacancies (in the first case) or with donor complex formations (in the second one). It has been shown that in the vacancy-doped p-Cd$_x$Hg$_{1-x}$Te the effective diffusion coefficients for the mercury interstitials that determines the depth of the converted layer are equal each other at equal temperatures either under thermal annealing in the saturated mercury vapour or anodic oxide annealing. It proves the identity of the mercury concentration in the diffusion source. Absence of the conversion under anodic oxide annealing in the As-doped p-Cd$_x$Hg$_{1-x}$Te is explained by insufficient Hg concentration in the source and it matches well with necessary condition for donor complex formation as it takes place under IBM.

Keywords: Cd$_x$Hg$_{1-x}$Te, p-n structure, mercury diffusion, ion beam milling, anodic oxide and thermal annealing.

1. Introduction

The p-to-n type conductivity conversion in p-Cd$_x$Hg$_{1-x}$Te bulk crystals and epitaxial layers is one of the most important processes involved into material production and device fabrication [1]. Namely this explains why such great attention of researchers is drawn to the achievement of the necessary controllability of these processes, which requires thorough knowledge of the p-Cd$_x$Hg$_{1-x}$Te properties at atomic size.

Type conversion of conductivity in the vacancy-doped p-Cd$_x$Hg$_{1-x}$Te crystals (the crystals p-type of which is determined by its native acceptors – mercury vacancies V$_{Hg}$) is observed under thermal annealing (TA) in mercury vapour [2], under anodic oxide thermal annealing (AOA) [3], and under ion-beam milling (IBM) [4]. At that, there is no need for thermal activation of the process in the last case. In all these processes the conversion of type of conductivity is thought to be determined by the diffusion of mercury interstitials (HgI) from the respective surface source and their recombination with the cationic vacancies in the bulk. That is why all these processes have a number of common features [1]. For example, the value $D_{Hg} = l^2/t$ is the mercury diffusion effective coefficient (where $l$ is the depth of the p-n junction and $t$ is the process duration) can be used for characterisation of each process. This value is a constant in each of the processes under existing process conditions and material properties and it falls due to the initial Te excess increase in the material [1,3,5].

The p-to-n conversion under TA is the most investigated case among the processes considered above. A number of models have been proposed to explain its peculiarities [6–8]. The analysis of the results of these models applying to explain experimental data on mercury diffusion indicates the necessity to know in details the history of samples and conditions of the process. Especially, it concerns attempts to analyse type conductivity conversion in different processes in the framework of one certain model as it was done by Shaw and Capper [1], since generally experiments on the conversion had been carried out by different authors separately for each process type and on samples of different technological origin. Thus, the authors [1] have analysed experimental data [5] on the type conductivity conversion under IBM in homogeneous epitaxial layers of p-Cd$_x$Hg$_{1-x}$Te in the framework of the model [6] and found that conversion rate decreased when ion current density $j$ increased. However, experimental data [4,9,10] where the conversion depth is investigated versus $j$ show opposite
Conductivity type conversion in p-Cd\textsubscript{x}Hg\textsubscript{1–x}Te

dependence and this well agrees with the results of theoretical analysis of the conversion process under IBM [11]. The authors [1] have also analysed the experimental data on the conversion under AOA [3] in the frame of model [6] and come to the conclusion that the anodisation enhances the conversion rate in $3 \times 10^3$ and $5 \times 10^4$ times at annealing temperatures of 150°C and 180°C correspondingly in comparison with the same treatment in mercury vapour. Such rate of the conversion [1] is corresponding to the values for surface concentration of mercury interstitials about $10^{13}$ cm$^{-3}$, which exceeds effective Hg concentration in the source created under IBM with ion current density $j \sim 0.6$ mA/cm$^2$. However, the mechanism of creating such a source under anodic oxide annealing has not been explained in any way.

The p-to-n conversion in the vacancy-doped p-Cd\textsubscript{x}Hg\textsubscript{1–x}Te is not unique type of the process in this alloy. As it has been established, similar conversion took place also either in As doped p-Cd\textsubscript{x}Hg\textsubscript{1–x}Te under reactive ions etching [12,13] or As or Sb doped p-Cd\textsubscript{x}Hg\textsubscript{1–x}Te under IBM [14,15]. In all these samples, the mercury vacancies were absent that was achieved with the help of special annealing. A conversion mechanism for these cases was proposed in Refs. 14 and 15 and it was connected with such donor complexes forming: As (Sb) atom in the Te site – proposed in Refs. 14 and 15 and it was connected with such donor complexes forming: As (Sb) atom in the Te site – mercury interstitial atom. It allows to hope for an opportunity of construction of a general model for all types of the conversion mentioned above. However, further research is necessary to make definitive this conclusion.

That is why the aim of present work was the investigation of p-to-n type conductivity conversion processes under IBM and thermal anodic oxide annealing done on the identical samples of vacancy-doped and As doped p-CdHgTe and it gave a possibility to obtain new data on conversion mechanisms.

2. Experiment

Bulk crystals of vacancy-doped p-Cd\textsubscript{x}Hg\textsubscript{1–x}Te ($x = 0.21$) from JSC “Pure metals” (Svetlovodsk, Ukraine) have been grown by the modified Bridgmen method with the replenishment from the solid-state phase [16]. After the growth, the samples were homogenised by annealing at Hg-saturated conditions (832 K – 96 hours; 693 K – 48 hours). Mercury vacancy concentration in the samples ($N_A = 4.8 \times 10^{15}$ cm$^{-3}$) was inferred from data of Hall measurements at 77 K; heavy hole mobility was $\mu_{ph} = 500$ cm$^2$/V.s. Since the samples were homogeneous, it was considered, that $\Delta T_F = N_A$, where $\Delta T_F$ is the initial Te excess [17].

The samples of extrinsically doped p-CdHgTe from Lviv National University were As autodoped graded gap epitaxial layers grown by the evaporation-condensation-diffusion method on As doped (111) CdTe substrates [18]. The as-grown epitaxial layers were in-situ subjected to annealing at 593 K in the vapours of the mercury source at 573 K for removal of the vacancies. Thus, the hole concentration in these samples was determined by amount of extrinsic acceptors dopants. SIMS showed that the composition was uniform ($x = 0.22$) with the constant As concentration $N_{As} = 2 \times 10^{16}$ cm$^{-3}$ at the depth up to about 10 µm. According to Hall measurements at 77 K they were characterized by the next parameters: heavy hole concentration (which corresponded to As concentration) $p_h = N_A = 2 \times 10^{16}$ cm$^{-3}$, heavy hole mobility $\mu_{ph} = 410$ cm$^2$/V.s.

The IB (EIKO, Japan) etching system with Ar$^+$ ions was used to perform IBM under the following conditions: ion energy $E = 500$ eV, ion current density $j = 0.1$ mA/cm$^2$, and duration $t = 300$ s. The samples were anodised in standard ethylene glycol electrolyte in galvanostatic regime under the current density 0.1 mA/cm$^2$ oxide thickness was about 800 nm. Further, the samples were annealed in air at 428 K for 20 min. with the oxide being chemically removed in KOH solution after annealing.

Hall coefficient versus magnetic field was investigated at 77 K in the fields 0.01–1.5 T and analysed to characterise initial samples as well as after each stage of processing. Measurements were held according to a standard method on direct current in Van-der-Pauw configuration. The step-by-step etch technique was used to determine the conversion depth. The depth of the etched layer on the each stage was measured by the surface profile measuring system DEKTAK-IIA (Sloan), error in depth measurements did not exceed 10%.

3. Results and discussion

3.1. Vacancy-doped p-Cd\textsubscript{x}Hg\textsubscript{1–x}Te

The results of the sample investigation subjected to ion-beam milling are presented in Fig. 1. Curve 1 [$R_p(B) > 0$] corresponds to the initial sample and its appearance is typical for p-Cd\textsubscript{x}Hg\textsubscript{1–x}Te with hole concentration...
≤ 5×10¹⁵ cm⁻³. After IBM (curve 2), effective Hall coefficient was negative in all range of magnetic field. It indicates formation of an n-type layer of some thickness due to IBM process.

Six consequent steps of chemical etching (CE) with the measurement of conductivity and Hall coefficient magnetic field dependencies after each step were carried out to estimate the depth of p-to-n junction (see curves 3–7 in Fig. 1). Consequent steps of CE changed appearance of Hall coefficient magnetic field dependencies gradually from \( R_H(B) < 0 \) after IBM (curve 2) to \( R_H(B) > 0 \) after 5 steps of CE (curve 7). After the first four steps of chemical etching, Hall coefficient sign inversion was observed in the magnetic field dependencies \( R_H(B) \) as it was typical for two-layer p-n structure (curves 3–6). Such changes of the dependencies can be explained as follows. An n-type layer of certain thickness is created initially due to IBM, and then its thickness gradually decreased by chemical etching. After full removal of the n-type layer, no conversion has taken place.

Total thickness of the chemically etched layer was about 12 µm, taking into account accuracy of estimated thickness of the etched layers, and only after the sixth step of etching the initial appearance of Hall coefficient magnetic field dependence \( R_H(B) \) has been restored. Thus, n-type layer with the thickness \( l_f = 12 \) µm has been formed.

For analysis of rate of the conversion similarly to Ref. 1, let’s take the value of product \( N_A l_f^2 / f \) which at the conditions of our experiment (\( l_f = 12 \) µm, \( t = 300 \) s) equals: \( N_A l_f^2 / f = 1.6×10^7 \) cm⁻³ s⁻¹. It well agrees with estimations of this value found in Ref. 1 for experimental data [5] (\( 1.6×10^8 \) and \( 2.7×10^7 \) cm⁻³ s⁻¹ for ion current density under IBM 0.032 and 0.6 mA/cm² correspondingly). It shows a giant (approximately 10⁷ times) increasing of the Hg diffusion flux under IBM in comparison with its diffusion flux under annealing in the saturated mercury vapour at room temperature and it is a sequence of the IBM created mercury diffusion source of extremely high mercury concentration.

By evaluations done for experimental data [5], effective mercury interstitial concentration in the source is \( 10^{12} \) cm⁻³–\( 10^{13} \) cm⁻³.

A mechanism for acceleration of mercury diffusion under IBM has been proposed in Ref. 11, where a surface source with high effective Hg interstitial concentration (\( \sim 10^{12} \)–\( 10^{13} \) cm⁻³) for p-Cd₀.2Hg₀.8Te (\( x = 0.2 \)) at the typical current density under IBM was theoretically substantiated

\[
[Hg_I]_{eff}^{++} = \frac{jS}{ek_w} \ln \left( 1 + \frac{N_0}{\delta_0} \right) \exp \left[ \frac{-2e\Delta\phi}{kT} \right] \tag{1}
\]

where \( S \) is the thermal spike cross section area (\( S \sim 10^{-13} \) cm²), \( k_w \) is the reaction rate constant for \( Hg_I^{+} \) and mercury double vacancy annihilation, \( \delta_0 \) is the mercury deficit in subsurface defect layer (\( \delta_0 \sim 10^{19} \) cm⁻³), \( N_0 \) is the initial high-temperature point defect concentration in the destroyed by ion region (\( N_0 \sim 10^{22} \) cm⁻³), \( \Delta\phi = \phi(l) - \phi(0) \), the surface barrier potential; brackets denote the concentration of corresponding defects.

According to Eq. (1), the Hg concentration in the source is increasing with rising of ion current density and it corresponds to the experimental data from literature [4,9,10] which indicated about increasing of conversion depth with rising of ion current density, but it is contrary to the conclusions [1]. On the other hand, results of the theoretical calculation of the conversion depth \( l_f \) dependence on \( \text{Ar} \) ion fluence for \( \text{Cd}_0 \cdot \text{Hg}_{0.8} \cdot \text{Te} \) based on the model [11] with mercury diffusion source, Eq. (1), agree well with known experimental data [4,10,19,20]. This is presented in Fig. 2.

Anodic oxide annealing of the similar vacancy-doped p-Cd₀.2Hg₀.8Te sample at 428 K during 20 min caused the formation of the converted n-layer of thickness approximately 6 µm. The results of this investigation are presented in Fig. 2.

After creations of the anodic oxide film the sign inversion is observed in magnetic field dependencies of the Hall coefficient (see curve 2). It indicates creation of the converted n-type layer caused by in-built positive charge in the oxide, as it is usually considered. After the thermal annealing of the anodic oxide (curve 3) sign inversion \( R_H(B) \) takes place in strong magnetic fields because of increase in the effective thickness of the n-type layer due to mercury diffusion and annihilation with mercury vacancies. Correspondingly, after the removing of the anodic oxide decrease in the effective thickness of the n-type layer is observed because of removing the in-built positive charge of the anodic oxide (sign inversion \( R_H(B) \) takes place in intermediate magnetic field between two previous curves, see curve 4). As a result of 4 steps of the chemical etching (\( Ad = 6 \) µm), the n-layer caused by mercury diffusion was completely removed (see curves 5–8).

Opto-Electron. Rev., 11, no. 2, 2003 N.N. Berchenko 95
Thickness of the converted n-layer after anodic oxide annealing (6 µm) corresponds to the value for the effective mercury diffusion coefficient \( D^* \) is \( 3 \times 10^{-10} \) cm\(^2\)/s. On the other hand, according to experimental data [19] and mercury diffusion model [8] the depth of conversion in the vacancy-doped Cd\(_{0.78}\)Hg\(_{0.22}\)Te crystals under annealing in the saturated mercury vapour is defined by the next relationship

\[
D^*_H = \frac{l^2}{t} = \left( \Delta^* / \Delta_{Te} \right) \exp(-1.045 eV/k_B T) \text{ cm}^2 / \text{s}, \quad (2)
\]

where \( \Delta^* = 3.0 \times 10^{18} \) cm\(^{-3}\) and \( \Delta_{Te} \) is the initial Te excess in a sample.

Since \( \Delta_{Te} = N_A \) in the initial samples, \( D^*_H = 3.8 \times 10^{-10} \) cm\(^2\)/s at the conditions of the present experiment \( (T = 428 \text{ K}, t = 20 \text{ min.}) \) and it correlates well with found here value \( l^2/t \) after AOA. It means that the mercury diffusion source efficiency is the same either in the process of the AOA or TA in the saturated mercury vapours. In other words, there is free mercury under the anodic oxide. Most probably it is excess mercury forced out to an oxide-crystal interface during formation of the oxide, which forms inclusions of the second phase. This conclusion does not agree with the results [1], where the experimental data [3] analysis showed that under the anodic oxide annealing at similar conditions \( (423 \text{ K}) \) acceleration of the conversion rate in \( 3 \times 10^3 \) times comparing to the TA in saturated mercury vapours was observed. Most probably this fact is the consequence of the authors’ assumption [1] that there are tellurium precipitates in the investigated samples, though it does not follow unequivocally from Ref. 3 where both as-grown and annealed samples were investigated. Moreover, as concentration of active mercury vacancies in Ref. 3 was low \( (\text{about } 10^{16} \text{ cm}^{-3}) \) it is more probable, that the results just for the annealed samples were submitted there [3].

The results on p-n type conductivity conversion in this sample under IBM are laid down in details [14,15] and are presented in Fig. 4.

The conversion mechanism in this case was explained in Refs. 14 and 15 by forming of donor complexes: mercury interstitial atom – arsenic atom in Te site. The converted layer thickness was about \( 10-12 \) µm and it corresponds to the value \( l^2/t \) after AOA. It means that the mercury diffusion source efficiency is the same either in the process of the AOA or TA in the saturated mercury vapours. In other words, there is free mercury under the anodic oxide. Most probably it is excess mercury forced out to an oxide-crystal interface during formation of the oxide, which forms inclusions of the second phase. This conclusion does not agree with the results [1], where the experimental data [3] analysis showed that under the anodic oxide annealing at similar conditions \( (423 \text{ K}) \) acceleration of the conversion rate in \( 3 \times 10^3 \) times comparing to the TA in saturated mercury vapours was observed. Most probably this fact is the consequence of the authors’ assumption [1] that there are tellurium precipitates in the investigated samples, though it does not follow unequivocally from Ref. 3 where both as-grown and annealed samples were investigated. Moreover, as concentration of active mercury vacancies in Ref. 3 was low \( (\text{about } 10^{16} \text{ cm}^{-3}) \) it is more probable, that the results just for the annealed samples were submitted there [3].

The results on anodic oxide annealing research of the similar sample are presented in Fig. 5. Changes in magnetic field dependencies appearance in this sample are in principle similar to those for vacancy-doped material. However, type conductivity conversion has not been observed in the As-doped p-Cd\(_{x}\)Hg\(_{1-x}\)Te under anodic oxide annealing \( (l_f < 1 \mu m, \text{Fig. 5}) \).

This fact entirely agrees with conversion mechanism proposed for IBM in the As doped p-Cd\(_{x}\)Hg\(_{1-x}\)Te in Ref. 14. Really, though mercury can also diffuse outside the second phase under anodic oxide annealing, mercury interstitial concentration cannot exceed the equilibrium value which is approximately \( 10^9 \) cm\(^{-3}\) [21]. This value is too small to allow the complexes forming which can take place only while \( [Hg^{I^+}] \gg K \), where K is the reaction constant for the complex formation process: \( K = K_0 \exp(-\Delta H_c / k_B T) \). Here \( K_0 \approx 10^{22} \) cm\(^3\), \( \Delta H_c = 1 \text{ eV} \) – enthalpy of complex formation [14]. In our experiment, i.e., at 428 K, \( K \approx 10^{10} \) cm\(^{-3}\) \( [Hg^{I^+}] \) and separate replacement centres As\(_{Te}^+\) are the dominant defects. Therefore annealing of the sample

Fig. 3. Magnetic field dependencies for AOA vacancy-doped p-Cd\(_{x}\)Hg\(_{1-x}\)Te: 1– initial sample \( (R_H > 0) \); 2– after AOA; 3 – after thermal annealing of AO \( (T = 155^\circ C, t = 20 \text{ min.}) \); 4 – after removal of AO; 5–8 after each of 4 step-by-step chemical etching, (total removed layer thickness \( \Sigma d = 6 \mu m \)).

Fig. 4. Electron (solid line) and hole (dash line) concentration distributions at 77 K over the depth of Cd\(_{x}\)Hg\(_{1-x}\)Te:As epilayer subjected IBM.
with anodic oxide will not result in the donor complex formation and type conductivity conversion. It is one more confirmation of false conclusion [1] about acceleration of conversion rate at AOA.

4. Conclusions

Research of the type conductivity conversion in homogeneous samples of the vacancy-doped p-Cd$_x$Hg$_{1-x}$Te ($x=0.22$) under anodic oxide annealing gives the value for mercury diffusion effective coefficient that agrees well with the one for the annealing in the saturated mercury vapours at the same temperatures. It shows that the mercury diffusion source is identical in both cases. In the case with the anodic oxide it can be free mercury created during the oxidation process and then forced out on the oxide-crystal interface. Conclusion [1] concerning the conversion acceleration in $3\times10^3$ times under anodic oxide annealing in comparison with the thermal annealing in the saturated mercury vapours is most probably connected with the authors’ assumption [1] of tellurium precipitates existence in the investigated samples. The value of the mercury diffusion effective coefficient under the ion-beam milling in the vacancy-doped and As-doped p-Cd$_x$Hg$_{1-x}$Te well correlates with known in the literature experimental data and shows giant acceleration of the mercury diffusion flow comparing to the thermal annealing in the saturated mercury vapours. According to the proposed in Ref. 11, mechanism for mercury diffusion acceleration under IBM mercury concentration in the diffusion source increases when ion current density grows up and corresponds to the experimental data. Absence of the conversion under the anodic oxide annealing in the As-doped p-Cd$_x$Hg$_{1-x}$Te is explained by the fact that Hg concentration in the source is insufficient and it well correlates with the necessary condition for donor complexes forming: $[\text{Hg}^{\bullet\bullet}] >> K$, when it takes place under ion-beam milling.

References

8. V.V. Bogoboyashchy, “Study of distribution of mercury vacancies in Hg$_{0.8}$Cd$_{0.2}$Te”, Functional Materials. 8, 609–614 (2001).
16. V.V. Bogoboyashchii, K.R. Kurbanov, and A.P. Oksanich, “Industrial production of GaAs and \( \text{Hg}_{1-x}\text{Cd}_x\text{Te} \) based crystals and epitaxial structures in Ukraine: actuality and development outlook”, *Functional materials* 7, 546–551 (2000).

17. H.R. Vydyanath, “Lattice defects in semiconducting \( \text{Hg}_{1-x}\text{Cd}_x\text{Te} \) alloys. 1. Defect structure of undoped and copper doped \( \text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te} \)”, *J. Electrochem. Soc.* 128, 2609–2619 (1981).


19. V.I. Ivanov-Omskii, K.E. Mironov, and K.D. Mynbaev, “\( \text{Cd}_x\text{Hg}_{1-x}\text{Te} \) electrical properties under ion-beam milling”, *Fiz. Tekh. Polup.* 24, 2222–2224 (1990).


21. V.V. Bogoboyashchii, “Equilibrium intrinsic defects concentration in \( \text{Hg}_{1-x}\text{Cd}_x\text{Te} \) narrow gap compounds via data of galvanomagnetic and optical measurements”, *Cond. Media & Interfaces* 2, 132–137 (2000).