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MECHANISM FOR CONVERSION OF THE CONDUCTIVITY TYPE IN ARSENIC-DOPED p-$Cd_xHg_{1-x}Te$ SUBJECT TO IONIC ETCHING

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Based on an analysis of chemical diffusion of mercury in p-$Cd_xHg_{1-x}Te$:As *narrow-band solid solutions, a mechanism for conversion of the conductivity type upon ionic etching is suggested. It is shown that the n–p conversion of the conductivity in this case is due to the formation of a donor complex between arsenic in the* Te *sublattice and an interstitial* Hg *atom. Moreover, the electron concentration in the converted layer corresponds to the concentration of the implanted arsenic impurity. The theoretical results are confirmed by the experimental investigation of the electron concentration distribution over the n-layer of a* p-$Cd_xHg_{1-x}Te$:As *epistructure converted upon ionic etching.*

INTRODUCTION

At present the *n-p* conversion of the conductivity type in vacancy-doped p-$Cd_xHg_{1-x}Te$ (CHT) subject to ionic or plasma etching (IE or PE) has already been proved [1–9]. The general behavior of the properties of vacancy-doped p-$Cd_xHg_{1-x}Te$ subject to etching has also been well studied experimentally. As was demonstrated, after IE [1–6] or PE [7, 9] the *n-p* conversion of the conductivity type was observed to a certain depth determined by the ion fluence, the acceptor (Hg vacancy) concentration in the parent material, the composition of the solid solution, and the temperature of the sample subjected to treatment.

The conversion of the conductivity type in vacancy-doped p-$Cd_xHg_{1-x}Te$ subject to etching is connected with the recombination of residual intrinsic acceptor defects – mercury vacancies (V_{Hg}) – with interstitial mercury atoms (Hg_I) generated in abundance in the subsurface region of the crystal subject to ion bombardment and diffused into its depth. The most typical feature of such conversion is a superhigh mercury diffusion rate (the mercury diffusion front acceleration is about 10^5 times that higher than that recorded for annealing in Hg vapors). Superhigh Hg diffusion rates upon bombardment of vacancy-doped p-$Cd_xHg_{1-x}Te$ by low-energy particles in the process of IE were thoroughly examined in [10, 11]. Possible mechanisms of this phenomenon, which allowed qualitative and quantitative agreement with the experimental data to be obtained, were suggested there.

The *n-p* conversion in As-doped p-$Cd_{0.3}Hg_{0.7}Te$ [12, 13] and Au-doped p-$Cd_{0.3}Hg_{0.7}Te$ epilayers [14] subject to jet ionic etching (JIE) has been reported recently. Smith et al. [12] and Siliquini et al. [13] used the laser beam induced current (LBIC) technique to establish conversion. In so doing, they did not study in detail the physical characteristics of converted layers; the concentration of carriers in the *n*-converted layer was determined by comparison of the theoretical and experimental LBIC signal waveforms. Antoszewski et al. [14], based on an analysis of the physical characteristics of the converted *n*-layer, concluded that the conversion of the conductivity type in this case was caused by the diffusion processes. Nevertheless, no mechanisms for conversion of the conductivity type were suggested in the above-indicated works. This calls for new experimental and analytical investigations into mechanisms of point defect interaction in this material.

In the present paper, the influence of ionic etching on the electrophysical characteristics of As-doped p-$Cd_xHg_{1-x}Te$ epilayers is examined, and a possible mechanism for the *n-p* conversion of the conductivity type upon such treatment is suggested.

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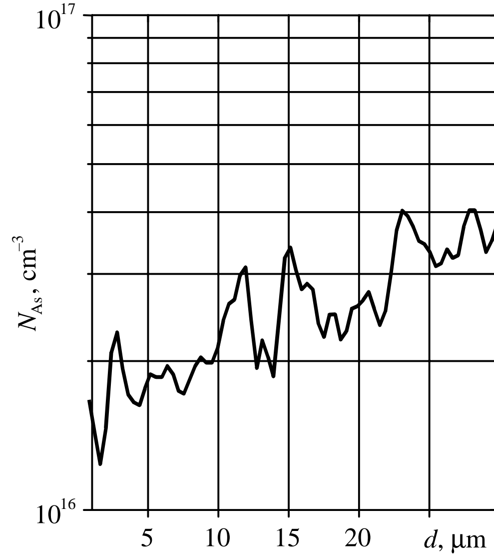

Fig. 1. Arsenic impurity distribution with thickness of the epilayer from the SIMS data.

1. EXPERIMENTAL RESULTS

In the present work, we study As–self-doped variband p-$Cd_xHg_{1-x}Te$ epilayers grown by the evaporation-condensation-diffusion method on CdTe(111) substrates at a temperature of 873 K [15]. CdTe substrates grown by the Bridgeman method with an implanted As impurity whose concentration was $N_{As} \sim (2–5)\cdot10^{16}$ cm^{-3} were used for doping. The epilayers grown were subject to *in situ* low-temperature isothermal annealing in mercury vapor (593/573 K) to minimize the concentration of mercury vacancies. The CHT epilayer sample examined in the present work was a monocrystal, and according to the data of its optical transmission at 300 K, its composition near the surface corresponded to $x = 0.22$.

The concentration of implanted arsenic impurity was determined from the data of secondary ionic mass spectroscopy (SIMS) (Fig. 1). It can be seen that within 10 µm, the As distribution over the CHT epilayer cross section can be considered uniform, with an As concentration of $1.8\cdot10^{16}$ cm^{-3}. The same measurements showed that the effective thickness of the variband layer was 100 µm, and the composition of the solid solution remained practically unchanged to a depth of 10 µm under the sample surface. Measurements of the electrophysical characteristics of the epilayer have shown that at 77 K the sample had p-type of conductivity with a hole concentration of $1.9\cdot10^{16}$ cm^{-3} and a mobility of 410 cm^2/(V·s). Thus, it follows that the p-type of conductivity of the examined sample is due to the presence of arsenic impurity rather then mercury vacancies; moreover, the implanted arsenic impurity possesses a 100% electrical activity in the epilayer.

The IB-3 facility made in EIKO (Japan) was used for IE by Ar^+ ions in the following regimes: energy of Ar^+ ions $E = 500$ eV, current density $j = 0.1$ mA/cm^2, and etching time 5 min, which corresponded to ion fluence $\Phi = 1.9\cdot10^{17}$ cm^{-2}. In so doing, the temperature of the samples was increased by no more than 20 K. To describe the samples before and after IE, the conductivity and the field dependences of the Hall coefficient were measured in magnetic fields up to 1.3 T using the standard dc procedure of Van der Pauws' method at 77 K. To determine the carrier distribution with thickness of the sample, we measured integral field dependences of the Hall coefficient and the sample conductivity after successive level-by-level chemical etching of the sample and subsequently calculated the Hall coefficient, conductivity, and mobility of carriers in the etched layer. These quantities were assumed constant for the etched layer, and the carrier concentration and mobility distributions with thickness of the sample were constructed based on these data.

Chemical etching was conducted in a Br_2 solution in butanol with subsequent washing in distilled methyl alcohol and deionized water. Before chemical etching, the contacts deposited on the sample were covered by a chemically-resistant

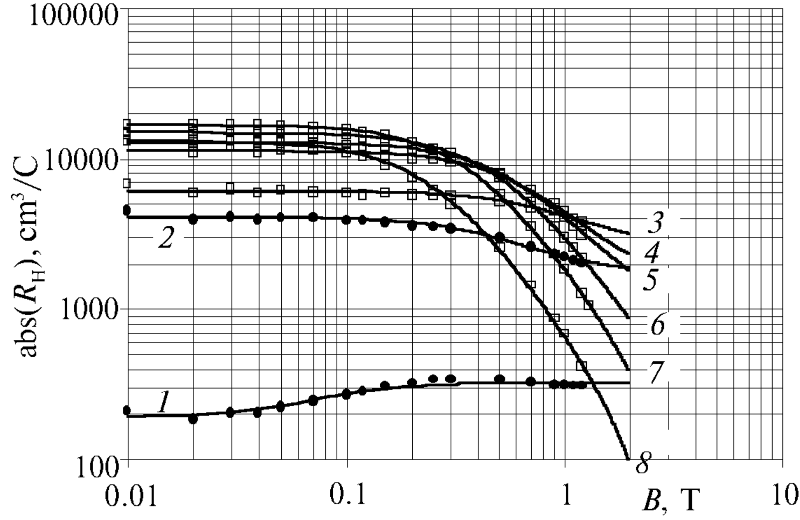

Fig. 2. Field dependences of the Hall coefficient R_H at 77 K for the initial sample (curve *1*, $R_H > 0$), after IE (curve *2*, $R_H < 0$), and after successive (1–6) chemical etchings (curves *3*–*8*, $R_H < 0$). Dots show the experimental data and solid curves show the results of calculations within the framework of the two-band model

varnish. The thickness of the etched layer was controlled by the etching time and was determined as the height of the step near the contacts measured with an interference microscope. This refined procedure has allowed us to conduct successive controllable chemical etchings with a step of ~1 ± 0.1 μm.

To calculate the Hall coefficient, conductivity, and mobility of carriers in the etched layer, we used the following relations:

$$\sigma = \frac{\sigma_{n+1} d_{n+1} - \sigma_n d_n}{d_{n+1} - d_n}, \tag{1}$$

$$R_H = \frac{\sigma_{n+1}^2 R_{H_{n+1}} d_{n+1} - \sigma_n^2 R_{H_n} d_n}{\left(\sigma_{n+1} d_{n+1} - \sigma_n d_n\right)^2} \left(d_{n+1} - d_n\right), \tag{2}$$

$$\mu_H = R_H \sigma, \tag{3}$$

where σ, R_H, and μ_H are the conductivity, Hall coefficient, and mobility in the etched layer, respectively; σ_{n+1} and σ_n are the total conductivities of the sample before and after etching, respectively; $R_{H_{n+1}}$ and R_{H_n} are the total Hall coefficients of the sample before and after etching, respectively; d_{n+1} and d_n are the sample thicknesses before and after etching, respectively.

Figure 2 shows the results of investigations into the field dependence of the Hall coefficient for the initial sample, after ionic etching, and after each step of chemical etching. As can be seen from the figure (curves *1* and *2*), after ionic etching the Hall coefficient has become negative for the entire range of the examined magnetic fields. This testifies to the formation of the layer with the *n*-type conductivity on the sample surface subject to IE. After successive level-by-level etchings (curves *3*–*8*), the field dependence of the Hall coefficient gradually changes its sign. This agrees with gradual thinning of the *n*-layer formed after IE and hence with the reduced contribution of electrons to the conductivity and the Hall effect.

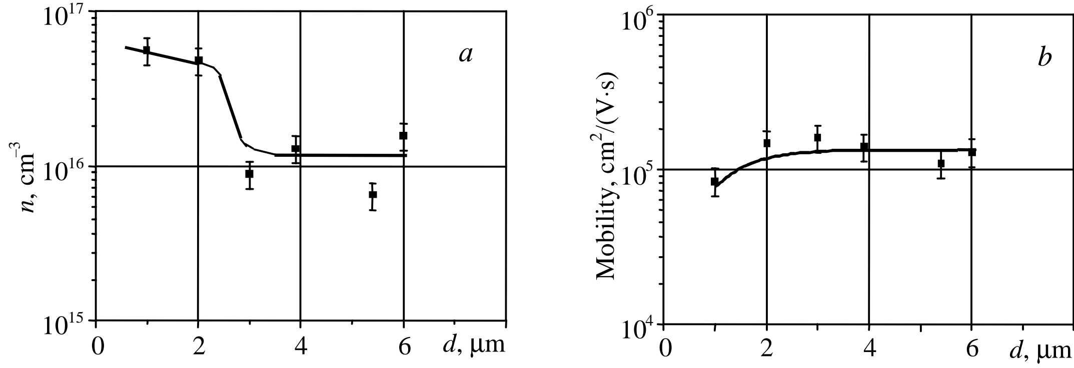

Fig. 3. Electron concentration (*a*) and mobility (*b*) distributions (77 K) with thickness of the CdHgTe:As epilayer subject to ionic etching.

After six level-by-level chemical etchings, a layer with a total thickness of about 6 μm was removed, that is, we investigated the region of the $Cd_xHg_{1-x}Te$ sample in which the composition x and the concentration of As impurity remained unchanged.

Figure 3 shows the electron concentration and mobility distributions determined by level-by-level chemical etchings.

As follows from Fig. 3, the character of changes of the physical characteristics of vacancy-doped $Cd_xHg_{1-x}Te$ subject to ionic etching is also retained for arsenic-doped $Cd_xHg_{1-x}Te$. In particular, in a thin subsurface layer 2–3 μm thick the electron concentration decreases rapidly with increasing depth; at greater depths (in the bulk of the n-layer), it remains unchanged [4]. The region of graded concentration is characterized by the enhanced concentration of electrons and their low mobility; it corresponds to the affected layer formed upon bombardment. The existence of this layer was confirmed by the data of x-ray investigations [9].

However, the electron concentration in the bulk of the converted n-layer of $Cd_xHg_{1-x}Te$:As is $1–1.5\cdot10^{16}$ cm^{-3}, that is, it significantly exceeds (by an order of magnitude and even more) the electron concentration ($10^{14}–10^{15}$ cm^{-3}) conventionally observed in vacancy-doped $Cd_xHg_{1-x}Te$. On the other hand, the electron concentration in the bulk of the n-layer of doped $Cd_xHg_{1-x}Te$ subject to ionic etching corresponds to the arsenic concentration in the layer before IE within the limits of the experimental error. The analogous regularity can be obtained if we analyze the results of [13]. This suggests that in this case the electron concentration is associated with donor complexes formed by interstitial mercury atoms released on the surface subject to IE and diffusing into the sample depth and As atoms in the Te sublattice.

2. MODEL

As demonstrated previously in [10, 11], three layers arise in a $Cd_xHg_{1-x}Te$ crystal upon bombardment by low-energy ions: the thin subsurface defect layer, the interlayer containing nonequilibrium point defects (the diffusion zone), and the unchanged inner crystal core. The ions striking the sample surface produce many nonequilibrium point defects in the defect zone. The most mobile defects (interstitial mercury atoms Hg_I and crowdions) penetrate into the diffusion zone creating there a considerable surplus of the nonequilibrium interstitial Hg atoms. In particular, for the diffusion mechanism of mercury penetration into the diffusion zone the average concentration of Hg_I at the interface with the defect layer ($z = 0$) has the form

$$\left[\mathrm{Hg}_I^{\cdot\cdot}\right]_0 = \frac{jS}{ek_{F0}} \ln\left(1 + \frac{N_0}{\delta_0}\right), \tag{4}$$

where j is the current density in the ion beam, S is the effective area of the thermal wedge tip ($S \sim 10^{-13}$ cm^2), N_0 is the density of sites in the metal sublattice, δ_0 is the Hg deficit in the defect layer, and k_{F0} is the annihilation rate constant for vacancies and interstitial Hg atoms. As shown in [11], the surface concentration of Hg_I reaches about 10^{12} cm^{-3} for $j \sim 10^{-4}$ A/cm^2. It exceeds by many orders of magnitude its value in equilibrium with fluid mercury at the same temperature.

Redundant Hg_I atoms migrate into the crystal depth and interact with free mercury vacancies V_{Hg} in the diffusion zone. As a result, the vacancies V_{Hg} completely vanish from this zone [11]. It is natural to assume that the surplus Hg_I atoms may also interact with other point defects, for example, to form complexes with impurity atoms. Indeed, according to the Le Chatelier–Braun principle, if heat is released in the process of complexing, the tendency to complexing should be especially strong at low temperatures.

In the initial p-$Cd_xHg_{1-x}Te$:As crystals, arsenic creates predominantly acceptor centers and hence is localized at sites of the Te sublattice. This substitution center (As_X) has one unpaired electron. For this reason, when an interstitial mercury atom with two valence unpaired electrons turns out to be nearby, these two defects can form a stable donor complex $Hg_I^{\cdot\cdot} - As_X'$ through a new chemical bond. For brevity, we designate this complex by the symbol $D^{\cdot}$. The corresponding reaction is written in the form

$$Hg_I^{\cdot\cdot} + As_X' \rightarrow D^{\cdot}. \tag{5}$$

The law of mass action

$$\left[Hg_I^{\cdot\cdot}\right] \cdot \left[As_X'\right] = K\left[D^{\cdot}\right] \tag{6}$$

corresponds to this reaction, where $K = K_0 \exp(-\Delta H_c/k_B T)$ is the equilibrium constant ($K_0 \sim N_0$ and ΔH_c is the combining heat).

Condition (6) should be supplemented by the condition of conservation of arsenic mass $[\,As\,]_{tot}$ dissolved in the crystal matrix:

$$[\,As_X'\,] + [\,D^{\cdot}\,] = [\,As\,]_{tot}. \tag{7}$$

Equation (7) is written under the assumption that the amount of As in interstices is negligible taking into account that all the acceptor As_X' substitution centers are ionized at room temperature.

Then from conditions (6) and (7) we obtain

$$\left[D^{\cdot}\right] = \frac{\left[Hg_I^{\cdot\cdot}\right]}{\left[Hg_I^{\cdot\cdot}\right] + K}\left[As\right]_{tot}. \tag{8}$$

It can be seen that, for $[\,Hg_I^{\cdot\cdot}\,] << K$, isolated As_X' substitution centers predominate, whereas for $[\,Hg_I^{\cdot\cdot}\,] >> K$, their complexes with $Hg_I^{\cdot\cdot}$ prevail. Moreover, the dominant species of dissolved arsenic is determined by the combining heat ΔH_c. It can be easily calculated that if $\Delta H_c > 0.6$ eV, dissolved arsenic will form complexes mainly with $Hg_I^{\cdot\cdot}$ at room temperature ($T_0 \sim 300$ K) for $[\,Hg_I\,] \sim 10^{12}$ cm^{-3}.

In the first approximation, ΔH_c can be identified with the Hg–As bond energy, neglecting the combining relaxation of the lattice. Unfortunately, combinations of Hg and As are poorly known; therefore, the exact value of this energy is not known as well. Nevertheless, it can be estimated as the dissociation energy of a Hg_3As_2 molecule with a pair of valence electrons:

$$\Delta H_c \approx \frac{1}{6} D_{Hg_3As_2}, \tag{9}$$

because in this compound both elements have the required valence.

According to [16], the molecular dissociation energy is equal to the difference between the energy of atomization of the compound and the energy of its congruent sublimation:

$$D_{\mathrm{Hg_3As_2}} = \Omega_{\mathrm{Hg_3As_2}} - S_{\mathrm{Hg_3As_2}} . \tag{10}$$

Here $\Omega_{\mathrm{Hg_3As_2}}$ can be estimated with fairly good accuracy from the known energies of atomization of Cd_3As_2 and Zn_3As_2 compounds based on its monotonic dependence on the serial number of elements of one group [16] using the equation

$$\Omega_{A_3B_2} = 3\Omega_A + 2\Omega_B - \Delta H^0_{A_3B_2} \tag{11}$$

($\Delta H^0_{A_3B_2}$ is the enthalpy of forming A_3B_2 from simple elements, the symbol *A* denotes Zn, Cd or Hg, and the symbol *B* denotes As).

Our calculations were performed for the following input parameters [16, 17]: $\Omega_{\mathrm{Hg}} \approx 0.61$ eV, $\Omega_{\mathrm{Cd}} \approx 1.17$ eV, $\Omega_{\mathrm{Zn}} \approx 1.35$ eV, $\Omega_{\mathrm{As}} \approx 2.86$ eV, $\Delta H^0_{\mathrm{Zn_3As_2}} \approx 1.32$ eV, and $\Delta H^0_{\mathrm{Cd_3As_2}} = -0.63$ eV. The latter yields the estimate $\Omega_{\mathrm{Hg_3As_2}} \approx 8.7$ eV. Then, assuming the relative stability of the solid phase of A_3B_2-type compounds and considering that the sublimation heat for $S_{\mathrm{Hg_3As_2}}$ takes an intermediate value of 2–3 eV, from Eqs. (9) and (10) we obtain $\Delta H_c \approx 1 \pm 0.1$ eV.

Thus, the combining energy for the $\mathrm{Hg}_I^{\cdot\cdot} - \mathrm{As}'_X$ complex is rather high; therefore, the combining processes in the diffusion zone should be taken into account in the model of Hg diffusion into $Cd_xHg_{1-x}Te$:As crystals upon bombardment by low-energy ions.

We took the model examined in [10, 11] as a basic model of Hg chemical diffusion. For $Cd_xHg_{1-x}Te$:As crystals containing only an insignificant amount of mercury vacancies V''_{Hg}, the equation for the rate of change of the V''_{Hg} concentration and terms that describe the interaction between V''_{Hg} and $\mathrm{Hg}_I^{\cdot\cdot}$ can be omitted. Instead of them, the corresponding equations and terms for As'_X and $D^{\cdot}$ should be added to the model. We also neglect the displacement of the surface layer subject to IE, considering the etching rate to be small compared to the velocity of the *p-n* junction.

As a result, for $Cd_xHg_{1-x}Te$:As we obtain the following system of diffusion kinetics equations:

$$\begin{cases} \dfrac{\partial}{\partial t}\left[\mathrm{Hg}_I^{\cdot\cdot}\right] - D_I \dfrac{\partial}{\partial z}\left\{\dfrac{\partial}{\partial z}\left[\mathrm{Hg}_I^{\cdot\cdot}\right] + \dfrac{2e}{k_B T}\left[\mathrm{Hg}_I^{\cdot\cdot}\right]\dfrac{\partial\varphi}{\partial z}\right\} = \kappa\left(K\left[D^{\cdot}\right] - \left[\mathrm{Hg}_I^{\cdot\cdot}\right]\cdot\left[\mathrm{As}'_X\right]\right), \\ \dfrac{\partial}{\partial t}\left[\mathrm{As}'_X\right] = \kappa\left(K\left[D^{\cdot}\right] - \left[\mathrm{Hg}_I^{\cdot\cdot}\right]\cdot\left[\mathrm{As}'_X\right]\right), \\ \left[D^{\cdot}\right] + \left[\mathrm{As}'_X\right] = \left[\mathrm{As}\right]_{\mathrm{tot}}, \\ \dfrac{\partial^2\varphi}{\partial z^2} = \dfrac{e}{\varepsilon\varepsilon_0}\left(n - p + \left[\mathrm{As}'_X\right] - \left[D^{\cdot}\right] - 2\left[\mathrm{Hg}_I^{\cdot\cdot}\right]\right), \end{cases} \tag{12}$$

where φ is the electric potential.

In the derivation of Eqs. (12) we considered the As_X substitution centers to be fixed ($D_{\mathrm{As}} = 0$), because impurities of this group diffuse slowly [17].

The combination reaction for $\mathrm{Hg}_I^{\cdot\cdot} - \mathrm{As}'_X$ is similar in many respects to the reaction of annihilation of $\mathrm{Hg}_I^{\cdot\cdot}$ and V''_{Hg}. It differs only in the fact that to form a new chemical bond of the complex, a certain potential barrier should be overcome. For this reason, according to [18], the rate constant of the combination reaction in this case can be written in the form

$$\kappa = \kappa_0 \exp\left(-\frac{E_a}{k_B T}\right), \tag{13}$$

where $\kappa_0 = 4\pi R(D_I + D_{As}) = 4\pi R D_I$ because $D_{As} = 0$. Here R is the capture radius, and for oppositely charged centers $R \sim r_D$ (r_D is the screening radius) [18]. Comparing expressions for κ_0 and k_F (the annihilation rate constant for $Hg_I^{\cdot\cdot}$ and V_{Hg}'' [11]), we easily obtain that $\kappa_0 \sim k_F$.

The system of equations (12) is rather complicated. In this case, one must resort to the method of stationary concentrations and analyze various limiting cases (see [11]).

Let us assume that the stage of complexing is rapid ($\kappa l^2[As]_{tot} >> D_I$), and the process as a whole is limited by mercury diffusion. In this case, according to the method of stationary concentrations, the first equation of system (12) must be replaced by its difference with the second equation and equilibrium condition (6) must be used instead of the second equation of the system. Then, differentiating (6), the rate of change of $[As_X']$ can be found and subsequently substituted into the first equation newly obtained. As a result, taking advantage of the above estimates, according to which the inequality $K << [Hg_I^{\cdot\cdot}] << n_i$ is fulfilled in the diffusion zone, for this crystal region we derive the following system of equations:

$$\begin{cases} \left(1+\frac{K[As]_{tot}}{[Hg_I^{\cdot\cdot}]^2}\right)\frac{\partial}{\partial t}[Hg_I^{\cdot\cdot}] \approx D_I \frac{\partial}{\partial z}\left\{\frac{\partial}{\partial z}[Hg_I^{\cdot\cdot}] + \frac{2e}{k_B T}[Hg_I^{\cdot\cdot}]\frac{\partial\varphi}{\partial z}\right\}, \\ [As_X'] \approx \frac{K[As]_{tot}}{[Hg_I^{\cdot\cdot}]}, \\ [D^{\cdot}] \approx [As]_{tot}, \\ \frac{\partial^2\varphi}{\partial z^2} = \frac{e}{\varepsilon\varepsilon_0}\left(n - p - [As]_{tot}\right) . \end{cases} \tag{14}$$

Comparing Eq. (14) with the equations of diffusion kinetics obtained in [11] for $Cd_xHg_{1-x}Te$ crystals with vacancies, we easily see their complete analogy. Namely, all equations of system (14), except the third one, can be derived from the corresponding equations of [11] if we replace the equilibrium constant K_F by the product $K[As]_{tot}$, the concentration V_{Hg}'' by $[As_X']$, and the difference $n - p$ (in the equation for φ) by $n - p - [As]_{tot}$. This analogy allows one to easily generalize the conclusions of [11] to the case examined here given that the $Hg_I^{\cdot\cdot}$ concentration at $z = 0$ is not too high:

$$[Hg_I^{\cdot\cdot}]_0^2 << K[As]_{tot} . \tag{15}$$

As was demonstrated in [11], the quasistationary regime is established in the diffusion zone. In this regime, the $Hg_I^{\cdot\cdot}$ flux density remains practically the same throughout the diffusion zone. In addition, for sufficiently thick layers ($l >> r_D$) the influence of an electric field is reduced only to the renormalization of the boundary condition at $z = 0$ through the multiplication of the right side of Eq. (14) into $\exp(-2e\Delta\varphi/k_BT_0)$, where $\Delta\varphi = \varphi(l) - \varphi(0)$. Therefore, the diffusion front in this case will be at the depth

$$l = \sqrt{\frac{2S\Phi D_I}{k_{F0}[As]_{tot}} \ln\left(1+\frac{N_0}{\delta_0}\right)} \exp\left(-\frac{e\Delta\varphi}{k_B T_0}\right) \tag{16}$$

for the diffusion mechanism of $Hg_I^{\cdot\cdot}$ penetration from the defect layer or at the depth

$$l = \sqrt{\frac{2\Phi \Delta N L^*}{[\text{As}]_{\text{tot}}}} \tag{17}$$

for the crowdion penetration mechanism. Here Φ is the ion fluence and expressions for L^* and ΔN are given in [11].

In the opposite case in which

$$\left[\text{Hg}_I^{\cdot\cdot}\right]_0^2 >> K\left[\text{As}\right]_{\text{tot}}, \tag{18}$$

the $\text{Hg}_I^{\cdot\cdot}$ atoms diffuse freely through the bulk of the diffusion layer and do not interact with impurities. In this situation, the $\text{Hg}_I^{\cdot\cdot}$ concentration in the diffusion layer obeys the conventional law

$$\left[\text{Hg}_I^{\cdot\cdot}\right] = \frac{jS}{ek_{F0}} \ln\left(1 + \frac{N_0}{\delta_0}\right) \exp\left(-\frac{2e\Delta\varphi}{k_\text{B}T_0}\right) \text{erfc}\left(\frac{z}{2\sqrt{D_I t}}\right). \tag{19}$$

Another limiting case in which Eq. (12) admits the method of stationary concentrations is a low complexing rate ($\kappa l^2[\text{As}]_{\text{tot}} << D_I$). In this case, the $\text{Hg}_I^{\cdot\cdot}$ atoms diffuse freely, and the stationary diffusate distribution is rapidly established in the crystal. Assuming that on the rear side of the plate (or at the epilayer-substrate interface) the equilibrium concentration $\text{Hg}_I^{\cdot\cdot}$ is equal to zero and considering that $K <<$ [$\text{Hg}_I^{\cdot\cdot}$] $<< n_i$ and $r_D << d$, we derive the new system of equations:

$$\begin{cases} \dfrac{\partial}{\partial z}\left(\dfrac{\partial}{\partial z}\left[\text{Hg}_I^{\cdot\cdot}\right] + \dfrac{2e}{k_\text{B}T}\left[\text{Hg}_I^{\cdot\cdot}\right]_0 \dfrac{\partial\varphi}{\partial z}\right) \approx 0\,, \\ \dfrac{\partial}{\partial t}\left[\text{As}'_X\right] + \kappa\left[\text{Hg}_I^{\cdot\cdot}\right]\cdot\left[\text{As}'_X\right] \approx \kappa K\left[\text{As}\right]_{\text{tot}}\,, \\ \left[D^\cdot\right] + \left[\text{As}'_X\right] = \left[\text{As}\right]_{\text{tot}}\,, \\ \dfrac{\partial^2\varphi}{\partial z^2} \approx \dfrac{e}{\varepsilon\varepsilon_0}\left(n - p + \left[\text{As}'_X\right] - \left[D^\cdot\right]\right)\,, \end{cases} \tag{20}$$

where d is the plate (epilayer) thickness. The time of establishing the stationary distribution is d^2/D_I in order of magnitude.

In this case, the first three equations of the system can be easily solved, and the system assumes the form

$$\begin{cases} \left[\text{Hg}_I^{\cdot\cdot}\right] \approx \left[\text{Hg}_I^{\cdot\cdot}\right]_0 \cdot \exp\left(-\dfrac{2e\Delta\varphi}{k_\text{B}T}\right)\cdot\left(1 - \dfrac{z}{d}\right), \\ \left[\text{As}'_X\right] \approx \left[\text{As}\right]_{\text{tot}} \exp\left(-\kappa\left[\text{Hg}_I^{\cdot\cdot}\right]\cdot t\right)\,, \\ \left[D^\cdot\right] \approx \left[\text{As}\right]_{\text{tot}}\left\{1 - \exp\left(-\kappa\left[\text{Hg}_I^{\cdot\cdot}\right]\cdot t\right)\right\}\,, \\ \dfrac{\partial^2\varphi}{\partial z^2} \approx \dfrac{e}{\varepsilon\varepsilon_0}\left(n - p + \left[\text{As}'_X\right] - \left[D^\cdot\right]\right)\,. \end{cases} \tag{21}$$

From here it follows that the p-n conversion front in this case is displaced into the crystal depth by the law

$$l = d \cdot \left(1 - \frac{\ln 2}{\kappa[\text{Hg}_I^{\cdot\cdot}]\cdot t}\right). \tag{22}$$

3. DISCUSSION OF THE RESULTS

The above-discussed model predicts the influence of some impurities, in particular As, on the kinetics of mercury diffusion upon bombardment of $Cd_xHg_{1-x}Te$ crystals by low-energy ions. This influence may be significant and observed experimentally when the bond energy of the complex As impurity – $Hg_I^{\cdot\cdot}$ is sufficiently high ($\Delta H_c > 0.6$ eV).

When the potential barrier to the formation of the chemical bond in the complex is low (namely, when $E_a < 0.5$ eV), the substitution centers will play the role of $Hg_I^{\cdot\cdot}$ traps and will decelerate the penetration of the diffusate into the crystal depth. Indeed, since at room temperature $D_I \sim 10^{-4}$ cm^2/s [11] and $r_D \sim 10^{-6}$ cm, then $\kappa_0 \sim 10^{-9}$ cm^3/s. This is a large value, and for $E_a < 0.5$ eV and diffusion layer thickness $l > 10^{-4}$ cm, the strong inequality $\kappa l^2[\mathrm{As}]_{tot} >> D_I$, corresponding to local equilibrium among As'_X, D, and $Hg_I^{\cdot\cdot}$ in the diffusion layer, is satisfied. This can be easily checked by comparing the diffusion term on the left side of the first equation of system (12) with terms on its right side.

The model suggests a change in the charge state of an impurity center after complexing. In particular, a singly charged acceptor As'_X will turn into a singly charged donor complex $Hg_I^{\cdot\cdot} - \mathrm{As}'_X$ denoted here by the symbol D, thereby leading to the *p-n* conversion of the conductivity type throughout the diffusion layer. Moreover, if the amount of uncontrollable impurities in the crystal is small compared to that of the doping additive, the impurity electron concentration in the *n*-zone will be close to the concentration of impurity holes before conversion. Exactly this result was obtained in our experiments on ionic etching and in [13].

Comparing our results with the data of [11], we can conclude that the conversion rates of doped and undoped p-$Cd_xHg_{1-x}Te$ crystals are close in order of magnitude at $[\mathrm{As}'_X] = [V''_{Hg}]$, if condition (15) is fulfilled simultaneously with the condition $\kappa t[\mathrm{As}]_{tot} >> 1$. They may differ only due to the contribution of the electric field, that is, $\Delta\varphi$. Namely, if the diffusion mechanism of $Hg_I^{\cdot\cdot}$ penetration dominates, the thickness of the diffusion layer formed upon bombardment of a doped crystal should be n_i/n times less. Here n is the free electron concentration in the *n*-layer of a doped sample. For the crowdion penetration mechanism, the difference may be even less.

This conclusion agrees with the experimental results reported in [13], where the special features of conversion of the conductivity type of undoped $Cd_{0.3}Hg_{0.7}Te$ crystals with mercury vacancies ($[V''_{Hg}] = 1.6\cdot10^{15}$ cm^{-3}) and As-doped $Cd_{0.3}Hg_{0.7}Te$ crystals ($[\mathrm{As}'_x] = 1.6\cdot10^{16}$ cm^{-3}) were compared. In the first case, the *p-n* junction was at a depth of 90 μm after jet ionic etching for an hour. In the second case, the position of *p-n* junction, unfortunately, was not determined in [13]. Nevertheless, the *n*-layer thickness there may be considered as exceeding the film thickness ($l > d \sim 10$ μm), because the photo-emf was absent at the center of the *n*-layer.

Thus, the main conclusions for the model examined here in the case of rapid complexing ($\kappa l^2[\mathrm{As}]_{tot} >> D_I$) and low nonequilibrium $Hg_I^{\cdot\cdot}$ concentration ($[Hg_I^{\cdot\cdot}]^2 << K[\mathrm{As}]_{tot}$) are experimentally confirmed, which is strong evidence in favor of the adequacy of the conversion mechanism suggested here.

As to other limiting cases (high $Hg_I^{\cdot\cdot}$ concentration and low complexing rate), most likely they disagree with the experiment. Indeed, in the first case the diffusion front motion would be determined solely by D_I, so that the diffusate ($Hg_I^{\cdot\cdot}$) will penetrate through the whole sample of thickness $d \sim 0.01$ cm already after the first several seconds of ionic treatment.

In the second case, complete conversion of an epilayer of thickness d into the *n*-type requires a time period $t >> (\kappa[Hg_i]_0)^{-1} >> (d^2/D_I)\cdot([\mathrm{As}]_{tot}/[Hg_I^{\cdot\cdot}]_0)$. For the experimental conditions reported in [12, 13] ($d \sim 10$ μm and $[\mathrm{As}]_{tot} \sim 10^{16}$ cm^{-3}), this time period is $t >> 10^3$ s, whereas the ionic treatment lasted only several tens of minutes.

In conclusion, we note that complexing may also influence the change in properties of n-$Cd_xHg_{1-x}Te$ upon ionic bombardment. Indeed, ion treatment should increase the impurity electron concentration by $\Delta n \approx 2N_{A5}$, where N_{A5} is the residual concentration of acceptors of the fifth group of the Periodic Table. Since in high-quality n-$Cd_xHg_{1-x}Te$ crystals $N_{A5} \sim 10^{14}$ cm^{-3} [19], $\Delta n \sim 10^{14}$ cm^{-3}. This was confirmed in [9]. Moreover, the mobility of the majority carriers and especially the lifetime of the minority charge carriers should considerably increase [19], which was also observed in [9].

CONCLUSIONS

The main regularities of the *n*-*p* conversion of the conductivity type in As-doped p-$Cd_xHg_{1-x}Te$ crystals subject to ionic etching are explained in terms of notions of chemical diffusion of mercury in this material. It is shown that the conversion of the conductivity type in As-doped p-$Cd_xHg_{1-x}Te$ subject to IE is due to the formation of donor complexes between arsenic in the Te sublattice and an interstitial mercury atom, which must dominate when the bond energy of the complex $\Delta H_c > 0.6$ eV. In this case, the electron concentration in the converted *n*-layer must correspond to the concentration of doping arsenic impurity in the solid solution. This fact is confirmed by the investigations of the electron density distribution with thickness in $Cd_xHg_{1-x}Te$ epifilms subject to etching. As shown here, for the doped material, the parameters of Hg diffusion (the thickness of the converted layer and the velocity of its penetration into the sample depth) are similar to those for vacancy-doped $Cd_xHg_{1-x}Te$.

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