Defect Structure Rebuilding by Ion Beam Milling of As and Sb Doped p-Hg$_{1-x}$Cd$_x$Te

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This study focuses on developing an understanding of the mechanisms of ion beam milling induced p-to-n conversion in extrinsically (As or Sb) doped p-Hg$_{1-x}$Cd$_x$Te with $x \approx 0.2$. The basis of modeling is the quasichemical approach and the model of superfast Hg interstitial atoms diffusion that has permitted to explain the similar conversion occurred in Hg vacancy-doped p-type Hg$_{1-x}$Cd$_x$Te. In an acceptor doped material a donor is generated due to the formation of a complex (of interstitial Hg atom and an As or Sb atom located in the Te site). This model provides reasonably good fits with the experimental results obtained for As and Sb doped Hg$_{1-x}$Cd$_x$Te epitaxial layers where the electron concentration in the converted n-layer corresponds to the concentration of the p-type dopants. Different efficiency of the conductivity conversion observed for As and Sb doped samples may be explained by different enthalpy of complex formation calculated for As$_{Te}$–Hg$_I$ and Sb$_{Te}$–Hg$_I$ pairs.

Introduction The dry etching techniques such as ion beam milling (IBM) and reactive ion etching (RIE) are an effective process to obtain high quality n-type layers on Hg vacancy-doped p-type Hg$_{1-x}$Cd$_x$Te material [1, 2]. The physical mechanism used to explain the conversion of this type is that during the etching process the Hg atoms are liberated near the surface. These atoms diffuse into the underlying p-type material interstitially and annihilate with the dominant native acceptors – Hg vacancies (V$_{Hg}$), resulting in residual uncompensated donors converting the region to n-type. The most striking feature of this process is the interstitial Hg superfast diffusion leading to unexpectedly large conversion depths during the IBM at room temperatures [3, 4]. Its exhaustive interpretation was recently published in [5] where it was demonstrated that the effective Hg interstitial surface concentration generated during IBM for typical IBM conditions is ranging from 10^{11} to 10^{12} cm^{-3}. That is by several factors of magnitude greater than values which feature the mercury-saturated conditions at the same temperature. However it was established that dry etching can induce p-to-n conversion even in extrinsically doped p-Hg$_{1-x}$Cd$_x$Te : As in which the Hg vacancies have been previously filled using routine mercury anneal [6]. It was proposed [7] that for new *n*-type doping mechanism in p-Hg$_{1-x}$Cd$_x$Te : As the pairing of an interstitial Hg atom with As

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atom located in anion sublattice is responsible. The main purpose of this article is the subsequent development of this model by extending it also to another element from group V–Sb.

Model of p-to-n Conversion of Extrinsically Doped p-Hg$_{1-x}$Cd$_x$Te   The existing models [8] cannot explain the donor formation during the IBM in the V-group element doped p-Hg$_{1-x}$Cd$_x$Te. The core of our analysis is the assumption that interstitial mercury atoms (Hg$_I^{\bullet\bullet}$) during the IBM can interact with other point defects too; for example, to form complexes with impurity atoms. In initial Hg$_{1-x}$Cd$_x$Te crystal atoms of V-group elements (we label them as A) are acceptors as they reside in the Te sublattice. A centre of this kind (A$_X^{'}$) has one unpaired electron, and if there is an interstitial Hg atom with two unpaired valence electrons in the nearby area, these two defects can form a stable donor complex Hg$_I^{\bullet\bullet} - A_X^{'}$ due to forming a new chemical binding. Below we shall mark a complex of this kind as D$^{\bullet}$. The relevant reaction is written as

$$\text{Hg}_I^{\bullet\bullet} + \text{A}_X^{'} \leftrightarrow \text{D}^{\bullet}. \tag{1}$$

The law of mass action corresponds to the reaction above:

$$[\text{Hg}_I^{\bullet\bullet}] \cdot [\text{A}_X^{'}] = K[\text{D}^{\bullet}], \tag{2}$$

where $K = K_0 \exp(-\Delta H_c/k_B T)$ is the the equilibrium constant ($K_0 \approx N_0$ the node density in a metal sublattice; ΔH_c the enthalpy of complex formation). Equation (2) should be added with a condition of a permanent V-group element amount $[\text{A}]_{\text{tot}}$ dissolved in the crystal matrix:

$$[\text{A}_X^{'}] + [\text{D}^{\bullet}] = [\text{A}]_{\text{tot}}, \tag{3}$$

taking into consideration that the amount of A in the interstitial is small, and A$_X^{'}$ acceptor replacement centers are ionizing at room temperature. In this case

$$[\text{D}^{\bullet}] = \frac{[\text{Hg}_I^{\bullet\bullet}]}{[\text{Hg}_I^{\bullet\bullet}] + K}\, [\text{A}]_{\text{tot}}. \tag{4}$$

It follows that when $[\text{Hg}_I^{\bullet\bullet}] \ll K$, separate (isolated) replacement centers A$_X^{'}$ prevail, while for $[\text{Hg}_I^{\bullet\bullet}] \gg K$, complexes of these centers with Hg$_I^{\bullet\bullet}$ are prevalent, with the dominant form of dissolved V-group element being determined by the enthalpy of complex formation ΔH_c. Calculations have demonstrated that at room temperature ($T_0 \approx 300$ K) and $[\text{Hg}_I^{\bullet\bullet}] \sim 10^{12}$ cm^{-3} (this value is reached under typical ion beam densities during the IBM [5]) if $\Delta H_c > 0.6$ eV, dissolved V-group elements will exist as complexes with Hg$_I^{\bullet\bullet}$.

The ΔH_c in Hg$_{1-x}$Cd$_x$Te : As was estimated in [7] as $\Delta H_c \approx 1 \pm 0.1$ eV. This value is large enough to take into consideration complex formation while developing the model of Hg diffusion in Hg$_{1-x}$Cd$_x$Te : As during the IBM. For Hg$_{1-x}$Cd$_x$Te : Sb this results in $\Delta H_c \approx 0.6$–0.9 eV. Thus, even though the Hg$_I^{\bullet\bullet} - Sb_X^{'}$ complex formation energy is less than that of the Hg$_I^{\bullet\bullet} - As_X^{'}$ complex, nevertheless, as it is greater than 0.6 eV this is sufficient to its formation at room temperature.

The diffusion kinetics equations in extrinsically doped materials are similar to the one for vacancy-doped p-Hg$_{1-x}$Cd$_x$Te [5], that allows to extend the conclusions [5] on an impurity-doped material. Under these conditions a diffusion front in the case of the

diffusion-type $Hg_I^{\bullet\bullet}$ penetration from the defect layer will be observed at the depth:

$$l = \sqrt{\frac{2SD_I}{k_{F0}[A]_{tot}} \ln\left(1 + \frac{N_0}{\delta_0}\right) \exp\left(-\frac{e\,\Delta\varphi}{k_B T_0}\right)}, \tag{5}$$

where $\Phi = j \cdot t/e$ is the ion dose; D_I the diffusion coefficient for $Hg_I^{\bullet\bullet}$; δ_0 the mercury deficiency inside the defect layer ($\sim 10^{19}$ cm^{-3}); S the area of the thermal spike cross section ($S \approx 10^{13}$ cm^2); and $\Delta\varphi = \varphi(l) - \varphi(0)$ the internal electric field.

Experimental Procedures and Results Two starting samples used in this study were As or Sb auto-doped p-$Hg_{1-x}Cd_xTe$ layers epitaxially grown by the evaporation–condensation–diffusion method on As or Sb doped (111) CdTe substrates correspondingly. The as-grown epitaxial layers were in-situ subjected to a standard low-temperature anneal in a saturated mercury atmosphere to fill Hg vacancies. For similar non-doped layers such an annealing type converts them to n-type due to the presence of residual donors ($N_D - N_A < 1 \times 10^{15}$ cm^{-3}). Thus the hole concentration in the samples before IBM (see Table 1) is defined by an amount of extrinsic p-type dopants. The layers were characterised by secondary ion mass spectroscopy (SIMS) depth profile measurements for doping and alloy composition profiles. The effective thickness of epitaxial layers with smoothly increasing composition is approximately 100 μm and 80 μm for layers doped with As and Sb, respectively. However, in the depth range of 10 μm from the surface the composition in both cases is uniform within the limits of the experimental accuracy and agrees well with the results of infrared transmission measurements presented in Table 1. Also the As and Sb profiles are uniform in this range.

The IB-3 (EIKO) etching system with Ar$^+$ ions was used to perform IBM under the following conditions: ion energy $E = 500$ eV, current density $j = 0.1$ mA/cm^2, duration $t = 5$ min.

The electrical properties of initial and ion-milled samples and the depth of p–n junction were measured at 77 K in magnetic fields between 0.01 and 1.5 T using the "step by step etch" technique. In this technique, semiconductor layers are sequentially stripped through chemical etching and the differential Hall effect and conductivity in the van der Pauw configuration are performed. The thickness of material removed at etching stage was measured, the results of this analysis are presented in Table 1. The concentration and mobility are presented only for majority carriers.

The main conclusions inferred from the table are the following. Above all it is seen that the both initial samples are p-type with the hole concentrations nearly equal the As and Sb concentrations given by SIMS. This agrees well with the well-known 100%

Table 1
Summary of the measured parameters

#	dopant	x	N_A (SIMS) (10^{16} cm^{-3})	before IBM		after IBM		
				p(77 K) (10^{16}cm^{-3})	μ(77 K) (cm^2/Vs)	l (μm)	n(77 K) (10^{16} cm^{-3})	μ(77 K) (cm^2/Vs)
1	As	0.22	2 ± 0.5	1.9	410	13	1.6	120 000
2	Sb	0.17	7 ± 2	7	630	4	1.0	350 000

incorporation of group-V elements as acceptors under mercury-saturated conditions. Then after IBM both samples changed their conductivity type on the depth close to the junction depth in the vacancy-doped p-$Hg_{1-x}Cd_x$Te. This permits to assume that these changes are also determined by super-fast mercury interstitial atom diffusion. In the As doped sample the electron concentration in the main part of converted n-layer is nearly equal to the hole concentration in the samples before IBM, and the As concentration as it is estimated by SIMS, i.e. the donor concentration is directly governed by the concentration of the p-type dopant. So, we suggest that p–n type conductivity conversion in the As doped sample during the IBM is due to the formation of As_{Te}–Hg_I pairs. However, for the Sb doped sample the donor concentration after IBM is smaller in comparison with the Sb concentration. We attribute this to the smaller enthalpy of Sb_{Te}–Hg_I pair formation, which is close to the critical energy. This can affect the efficiency of pair formation and further studies are necessary to get more details about the complex formation in $Hg_{1-x}Cd_x$Te : Sb.

Conclusions   Basic features of the n–p conductivity conversion in As and Sb doped p-$Hg_{1-x}Cd_x$Te during the ion beam milling are explained by the Hg chemical diffusion in this material. The main characteristics of Hg diffusion (the thickness of the converted layer and its widening rate) in the doped material are similar to those in vacancy-doped $Hg_{1-x}Cd_x$Te. It has been proved that the conductivity conversion is caused by the formation of $Hg_I^{\bullet\bullet} - A_X^{'}$ complexes which will be prevalent at the energy $\Delta H_c > 0.6$ eV, fast complex formation and low concentration of non-equilibrium mercury. Under these conditions the electron concentration in the main volume of the converted n-layer will correspond to the previous acceptor dopant concentration. This fact is convincingly confirmed by profiles of the electron concentration distribution in $Hg_{1-x}Cd_x$Te : As epitaxial layers after the IBM processing that is a strong argument for the proposed conversion mechanism, and further studies will lead to a final concept of the complex formation in $Hg_{1-x}Cd_x$Te : Sb.

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