MANIFESTATION OF THE LASER-SHOCK-WAVE-INDUCED DIFFUSION OF DOPANTS BELONGING TO THE FIRST GROUP OF ELEMENTS IN $Hg_{0.8}Cd_{0.2}Te$

V.S. YAKOVYNA, I.V. KURILO, N.N. BERCHENKO

Lviv Polytechnic National University
(12, Stepan Bandera Str., L'viv 79013, Ukraine)

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The influence of laser-induced shock waves (LISWs) on narrow-gap semiconductors with high nonequilibrium concentrations of dopants has been considered, with the structures $Hg_{0.8}Cd_{0.2}Te$/Me (Me = Cu, Au) being taken as an example. The possibility of the dopant diffusion stimulated by LISWs from a layer on the semiconductor surface, which is nonuniform by concentration, into the bulk of the specimen has been demonstrated. It has been confirmed that the rapid diffusion of dopants belonging to elements of the first group and possessing high concentrations is accompanied by the creation of new compounds.

1. Introduction

Despite the permanent search for alternative materials and instrument structures such as superlattices and Schottky barriers, a solid solution $Hg_{1-x}Cd_xTe$ and its analogs do and will remain the basic material for the creation of photodetectors in the 8—14-μm wavelength range for a long time [1–3]. In addition, those materials also possess extremely interesting physical properties [4].

For today, the effective technologies of both the growing of perfect single crystals and epitaxial layers of $Hg_{1-x}Cd_xTe$ and the creation of various instrument structures have been elaborated. Therefore, the basic problem that stands nowadays before researchers is the further improvement of the parameters of $Hg_{1-x}Cd_xTe$-based devices and the enhancement of their stability. This task cannot be fulfilled without a profound study of the processes of defect formation in bulk single crystals and epitaxial layers formed by this solid solution, as well as at its interfaces with insulators and metals. Challenging remains the searching for such methods and facilities to control the parameters of both initial materials and the structures fabricated on their basis which would allow one to improve the operational parameters of devices and their reliability.

It should be noted that, in the case of chalcogenides, these methods have to be as low-temperature as possible. Consequently, we studied the influence of the shock waves that were induced by a pulse of laser emission on the defect subsystem of the bulk single crystals of $Hg_{0.8}Cd_{0.2}Te$ solid solutions [5–7].

The most convenient way to excite shock waves in a solid is the laser irradiation of the latter with nano- and picosecond pulses. The irradiation of the solid surface with such pulses results in the formation of the thin layer of a vapor and a weakly ionized plasma near the surface. This layer is spreading into both media and drives the mechanical compression waves before itself. Owing to the nonlinear properties of the media, these waves, provided a certain criterion is fulfilled, become shock at some depth [8].

As was shown in works [6, 7], the LISW interacts most intensively with $Hg_{0.8}Cd_{0.2}Te$ crystals, provided that there is a plenty of defects in them. In addition, the LISW-stimulated diffusion of intrinsic point defects has been discovered. Therefore, this work aimed at studying the influence of the shock-wave treatment on the distribution of the concentration of impurities in $Hg_{0.8}Cd_{0.2}Te$.

2. Experimental Method

The specimens for researches were bulk $Hg_{0.8}Cd_{0.2}Te$ single crystals with thick films of copper and gold deposited onto the surface. These films were chemically precipitated onto the specimen surfaces by the reduction of copper from sulfate and gold from chloride. It should be noted that the behavior of the impurities was studied using the specimens that had been cut out from the same washer that was used for the fabrication of specimens for studying the influence of LISWs on the mechanical properties of a bulk material [5].

A LISW was created by irradiating the specimens at room temperature with the help of a GOS-1001 neodymium glass laser with a LiF-gate that operates in the Q-switched mode (the emission wavelength was 1.06 μm, the pulse duration 30 ns). In order to protect the semiconductor against the direct action of a laser, we used a 100-μm copper foil [5].

The investigation of the specimens was carried out by measuring the field dependences of the Hall coefficient and the microhardness [5] over a slanting microsection, as well as by the selective etching of the microsection surface.

The field dependences of the Hall effect were measured at 77 K. The data were analyzed in the framework of the two-band model, which takes into account the presence of current carriers of two types. The range of applied magnetic fields was 0.02—1.4 T.

The mechanical properties of $Hg_{0.8}Cd_{0.2}Te$ crystals before and after the LISW action were researched by the microindentation method making use of a PMT-3 device. The loading on an indentor was 0.2 N, which corresponded to a horizontal section of the "microhardness—loading" ($H_V - P$) characteristic. The durations of the loading, holding under a loading, and unloading ($t = 10$ s) were chosen on the basis of experimental data concerning the time dependences of microhardness $H_V - t$ [9]. Each microhardness value was determined by averaging over 10—20 measurements.

The dislocation pattern was revealed by etching the specimen surface using a selective etchant with the composition 5 CrO_3:10 HF:2 HCl:5 H_2O, which reveals "fresh" dislocations on the {110} surfaces of $Hg_{0.8}Cd_{0.2}Te$.

The slanting microsection was obtained by pulling specimens from a 0.75% solution of Br_2 in methanol.

In addition, we carried out the reference measurements of microhardness over the slanting microsection of a specimen without metal films which was subjected to the LISW action. It was established that such specimens are homogeneous as for the microhardness H_V (H_V being within the limits of 479—492 MPa), and no correlation with the measurement depth was monitored. Thus, the shock-wave treatment itself does not create any abrupt variations in the microhardness inward the specimen or the features of the etching patterns which are described below.

3. Experimental Results and Their Discussion

Numerous researches show that the doping actions of gold and copper are similar in many aspects, because both these elements create singly charged acceptors which replace mercury in the metal sublattice and possess high diffusion coefficients [10]. Provided the impurity concentration is high, there appear the precipitates of telluride of the corresponding metal. For example, it was shown in work [11] (in that work, similarly to our experiments, the diffusion from thick films precipitated onto the $Hg_{0.8}Cd_{0.2}Te$ surface was studied) that if the concentration of gold is high and the structures under consideration undergo the low-temperature annealing in saturated mercury vapors, the additional process of gettering of an impurity is observed. It manifests itself in the appearance of a great number of precipitates of golden color in the bulk of the crystal near the surface layer—bulk interface. The concentration of such precipitates was highest at the interface and decreased inward the crystal. Also the ensembles of precipitates at small-angle interfaces and block boundaries were observed. The authors of work [11] believed that those were the precipitates of gold telluride. This compound is obviously formed owing to the diffusion of gold from the surface through the surface layer, where it reacts with the precipitates of tellurium and dislocations. The basic difference between the penetrations of an impurity with low and high concentrations is that the former provokes only the redistribution of the impurity from one region of the specimen into another one, while during the latter, the formation of new compounds does take place as well.

First of all, consider the results of galvano-magnetic researches. The results simplest for the interpretation were obtained for specimens with precipitated copper. The parameters of the majority current carriers for such specimens are presented in the table. The tabular data testify to that the conversion of the conductivity type was observed even for the reference specimens, which had not undergone the LISW treatment and had been held at room temperature for a long time. It is in a good agreement with the very high (even at room temperature) diffusion coefficient of copper atoms in $Hg_{0.8}Cd_{0.2}Te$; according to the data of work [1], it amounts to 1.824×10^{-10} cm^2/s at 300 K. On the other hand, the concentration of acceptors determined from the Hall effect for all specimens which were subjected to the LISW action, turned out almost twice as high as that in the untreated specimens with the hole mobility remaining practically constant. This allows us to assert that the LISW assists in either the introduction of a greater amount of copper into the metal sublattice or the copper diffusion into the specimen depth. In addition, while measuring galvanomagnetic effects for all specimens with precipitated copper (both subjected to the LISW treatment and not), anomalously high noises were registered. We believe that such sources of noise as contacts and microcracks were practically excluded, because, under the condition that the measuring procedures were identical, no similar noises were monitored for other specimens — both the specimens with precipitated gold and tens of specimens without metal films. Therefore, we think that those noises can be explained by the effects at the interfaces between the matrix and various complexes formed by copper and matrix materials under conditions of the diffusion from a practically unexhausted source of impurities.

However, the analogous measurements for specimens with chemically precipitated gold showed that the electric parameters of specimens remained constant both before and after the LISW action within the limits of experimental accuracy. The conversion of the conductivity type for the reference specimen that was kept at 300 K without the LISW treatment did not occur. We connect this fact with the much lower diffusion coefficient of gold in $Hg_{0.8}Cd_{0.2}Te$ (6.651×10^{-13} cm^2/s at 300 K [1]) as compared to that of copper. The absence of variations of the parameters of current carriers after the LISW action testifies to that, contrary to the copper atoms, the gold ones do not enter as an electrically active impurity or the impurity concentration (and, accordingly, the depth of the converted layer) is rather small for not to manifest itself in the field dependences of the Hall coefficient.

Although the galvano-magnetic measurements have not registered the penetration of gold atoms being in an electrically active state, the patterns of selective etching of the slanting microsection and the microhardness measurement results along the microsection revealed certain variations under the action of the LISW.

We emphasize that the distribution of microhardness along the microsection is uniform for the reference specimen (not covered with metal films but subjected to the LISW action), with the average value of microhardness being 477 MPa. The selective etching pattern of the slanting microsection did not reveal any feature in this case.

But for specimens subjected to the LISW action, the selective etching revealed a clear-cut stripe of fine precipitates which disappeared completely (and rather abruptly) at a certain depth (Fig. 1). In the microscope field of vision, one can also notice the difference between the diagonal dimensions of the indentor imprints made in the region of precipitates and on the pure section of the surface. Really, for two researched specimens, H_V equals 518 and 531 MPa on the surface section with precipitates, whereas on the deeper section free from precipitates, $H_V = 475$ and 483 MPa, respectively.

We relate such results to the field of significant stresses caused by a high concentration of precipitations of the other phase. Really, H_V amounts to 521 MPa in the dislocation field created by the indentor after etching off the layer which contained the imprint (Fig. 2). At the same time, $H_V = 499 \div 501$ MPa even on the strongly scratched surface of the same specimen, which evidences for a much more stronger field of stresses created by precipitates and confirms the correctness of the conclusions made.

It should be noted that, in the case of gold penetration, the dimensions of precipitates were rather small (less than 0.5 μm), which prevented us from the microhardness measurements of the precipitates themselves.

Therefore, we guess that, under the action of the LISW, the penetration of gold took place from the deposited film into the bulk of the material, and, owing

Parameters of $Hg_{0.8}Cd_{0.2}Te$ specimens before and after diffusion of copper from the deposited layer

Specimen	LISW pressure, GPa	Conductivity type	σ, Ohm^{-1}·cm^{-1}	n, p, cm^{-3}	μ_n, μ_p, cm^2/(V·s)
Initial	—	n	2.87	1.17×10^{14}	150 000
Reference	—	p	0.975	1.67×10^{16}	375
Cu-1	2×1.04	p	1.63	2.55×10^{16}	245
Cu-2	1.06	p	1.68	2.84×10^{16}	220
Cu-3	2×0.87	p	1.53	2.49×10^{16}	250
Cu-4	1.5	p	1.42	2.37×10^{16}	265

Fig. 1. Stripe of fine precipitates on the slanting microsection of the specimen doped by gold with the imprints of the indentor

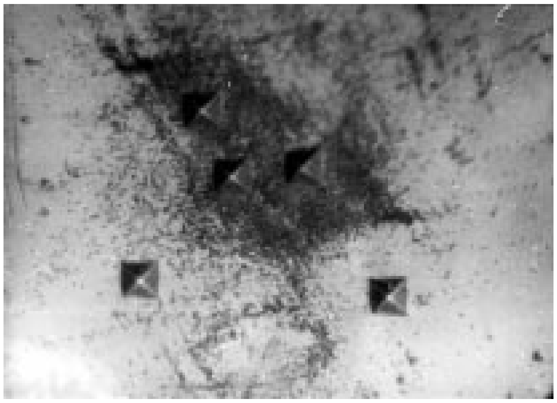

Fig. 2. Rosette at a depth revealed after etching off the layer, which contained the imprint, followed by the selective etching

to both the large gradient of pressure in the LISW front and the extremely nonequilibrium character of the process, the prevailing portion of gold enters in an electrically inactive state as the precipitates of another phase, the formation of which was described in work [11]. On the basis of the data from works [12, 13], one may suppose that this phase is most likely $AuTe_2$ possessing the microhardness within the interval 382 – 774 MPa [12], which does not contradict our results (we should notice that the compound Au_4Te_3 is unstable).

The other results of mechanical studies were obtained for specimens with deposited copper after the action of the LISW.

No attributes of the interfaces in the specimens with penetrated copper, similar to those in the specimens with gold, have been found. Instead, these specimens contained a great number of precipitates of another phase, the microhardness of which was 353 – 392 MPa. The general pattern of such precipitates is shown in Fig. 3. We notice that the arrangement of such precipitates is rather chaotic, which is connected first of all with the technological prehistory of each individual specimen, and reaches great depths (tens of micrometers). Similarly to the case with gold, we relate the precipitation of another phase, first of all, to the formation of copper telluride. In works [12, 14], three compounds in the Cu—Te system were described, namely, Cu_2Te, Cu_4Te_3, and CuTe, of which only Cu_2Te is stable up to the temperature of melting.

Taking into account the high concentrations of holes in the specimens after the diffusion of copper (see the table), one may take as obvious that the prevailing number of copper atoms enters into the metal sublattice as acceptors under the LISW action, contrary to gold ones, which, in our experiments, reached small depths, being mainly in the form of precipitates of another phase.

We explain such a difference, first of all, by distinctions between the processes of diffusion and LISW treatment resulted from the fact that the diffusion coefficient of copper in $Hg_{0.8}Cd_{0.2}Te$ is much greater than that of gold. Moreover, as the results of galvanomagnetic measurements show, copper diffuses at room temperature into $Hg_{0.8}Cd_{0.2}Te$ even without the LISW action. Therefore, the LISW treatment of specimens with the deposited copper layer was carried on when a great amount of copper had already diffused into the crystal under the action of temperature. Thus, in the case of specimens doped with copper, the LISW action has to be connected, first of all, with the destruction of copper-based complexes and associates (Fig. 3) and, to a lesser extent, with the diffusion of new portions of the impurity.

This conclusion is illustrated by a large number of rather big microporous precipitates (with the diameter up to 60 μm) with a low microhardness (as if the indentor falls into the cavities) and a fine-grained structure, which were observed only for the specimens subjected to the LISW treatment (Fig. 4). In our opinion, these microporous precipitates are the remnants of big copper-based complexes and associates that have been destroyed by the LISW, because no such precipitates were noticed in the reference specimen. Moreover, the destruction of the precipitates of another phase with a reduction of their relative volume is supported by the results of work [7].

It should be noted that the selective etching reveals the dislocation rosettes (Fig. 5) around the precipitates of copper telluride (Fig. 3), which is in a full agreement with the known data concerning the field of stresses

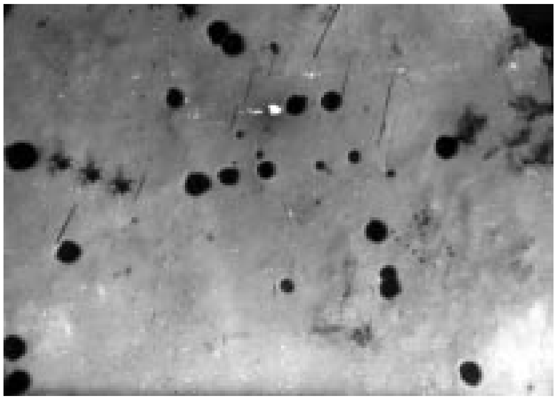

Fig. 3. The general view of the precipitates of another phase in specimens doped with copper

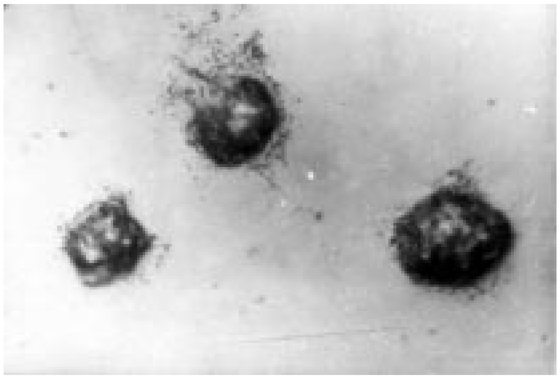

Fig. 5. Precipitates of another phase and the dislocation rosettes around them in specimens doped with copper

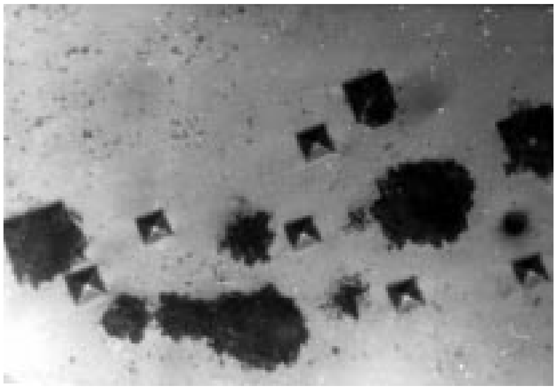

Fig. 4. Microporous precipitates with a fine-grained structure in specimens doped with copper

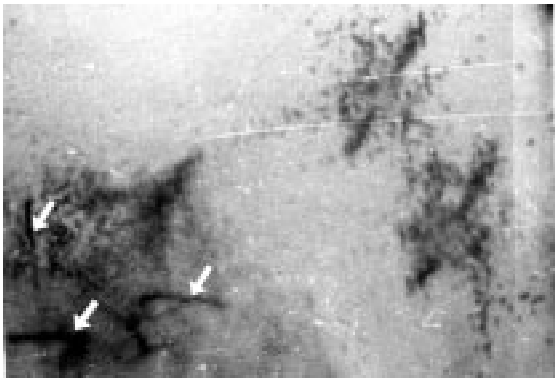

Fig. 6. Rosette at a depth, induced by the precipitate of another phase (the arrows point to microcracks)

around the precipitates of another phase. These stresses reach the amplitude close to the theoretical ultimate stress. For example, for the precipitates of SiC in Si, the components σ_{rr} and $\sigma_{\theta\theta}$ of the stress tensor are equal to $0.547G$ and $-0.273G$, respectively (G is the shear modulus of the matrix material) [14]. At the same time, for the precipitates of tellurium in CdTe, $\sigma_{rr} = 0.559G$ and $\sigma_{\theta\theta} = -0.279G$, while for the precipitates of tellurium in HgTe, these values amount to $0.566G$ and $-0.283G$, respectively [16]. Therefore, the calculated values of stresses on the precipitates' surface are close to the theoretical ultimate stress of the crystals under investigation. This is confirmed by the formation of cracks around the precipitates of another phase. For example, Fig. 6 illustrates a large dislocation rosette around the precipitate of another phase, which has been revealed after etching off the layer containing the precipitates (the arrows point to microcracks). One can neatly see that the pattern is similar to that of Fig. 2 which illustrates the dislocation rosette revealed after etching off the layer with an indentor imprint. We notice that the fields of stresses induced by the indentor and the precipitates of another phase differ by symmetry, because the strained states are different in those cases (the spherical precipitate and the pyramidal indentor).

To summarize, the results of this work confirm that the rapid diffusion of dopants, which belong to the first group of elements and possess a high concentration, results in the formation of new compounds (the tellurides of corresponding metals). It seems to be most probable that such compounds are formed more effectively under nonequilibrium conditions, e.g., provided the diffusion of an impurity with a high concentration, at high temperatures, or under the action of a large gradient of pressure, as it does in the shock-wave case.

4. Conclusions

The shock wave has been shown to reduce the number of macroscopic inhomogeneities of various types (precipitates and formations of another phase) in narrow-gap semiconductors $Hg_{1-x}Cd_xTe$. The LISW has been established to be an effective means for diminishing the specific volume of the precipitates of another phase.

For the first time, the possibility of the impurity diffusion stimulated by the LISW from the layer on the semiconductor surface, which is nonhomogeneous by concentration, into the bulk of the specimen has been demonstrated. Provided the rapid diffusion of impurities from the first groups of elements and with high concentrations, the formation of new compounds is probable.

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ПРОЯВИ СТИМУЛЬОВАНОЇ ЛАЗЕРНОЮ УДАРНОЮ ХВИЛЕЮ ДИФУЗІЇ ДОМІШОК ЕЛЕМЕНТІВ ПЕРШОЇ ГРУПИ В $Hg_{0,8}Cd_{0,2}Te$

В.С.Яковина, І.В.Курило, М.М.Берченко

Резюме

На прикладі структур $Hg_{0,8}Cd_{0,2}Te/Me$ (Me = Cu, Au) розглянуто результати досліджень впливу лазерних ударних хвиль на вузькощілинні напівпровідники за наявності високої нерівноважної концентрації домішок. Показано можливість стимульованої лазерною ударною хвилею дифузії домішок з неоднорідного за концентрацією шару на поверхні напівпровідника. Підтверджено, що при дифузії високої концентрації швидкодифундуючих домішок першої групи відбувається утворення нових сполук.