

# LASER STIMULATED CHANGES OF THE PHYSICAL PROPERTIES OF SOME SOLID STATE SOLUTIONS OF SEMICONDUCTORS A<sup>IV</sup>B<sup>VI</sup>

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## 1. Introduction

The problem of impurity and defect states in narrow-gap semiconductors of the group IV-VI (PbTe, PbSe, PbS) and their solid state solutions appears to be at present most important from the standpoint of a practical application of these materials. A great variety of experimental data on the effect that doping with various impurities has on the properties of IV-VI compounds [1] made it possible to ascertain that most of the impurity states can be explained in the model of localized states. These states can be treated as “deep states” both in the band gap and in the conduction or valence bands. There is special interest in the study of the behavior of paramagnetic impurities because the distribution and positions of magnetic ions in the lattice determine largely both the electronic and magnetic properties of these crystals. Lead telluride and lead selenide, doped with Mn and Eu, is the most thoroughly investigated compound of this group [2, 3]. It has been shown that manganese and europium in PbTe and PbSe are located mainly in the interstices and in inclusions containing the magnetic component, i.e., doping from the melt results in a highly nonuniform distribution of the impurity in the matrix.

On the other hand the interaction of IR laser radiation with semiconductor materials is of scientific interest. Investigations of the interaction of laser radiation with semiconductors are primarily concerned with the spectral region  $\hbar\omega > E_g$  (where  $E_g$  is the band gap,  $\hbar\omega$  is the photon energy of the laser radiation). This interaction results in a change in physical properties of near-surface layers, which is limited by the radiation effect zone [4].

The effect of laser IR radiation in the transparent region  $\hbar\omega < E_g$  on the properties of narrow-gap solid solutions  $Pb_{1-x}Sn_xTe$  and  $Pb_{1-x}Sn_xSe$  was studied in [5-7]. A change in the bulk electro-physical and optical properties was found. This is attributed mainly to a greater beating by laser radiation of inclusions which are present in crystals of these compounds [8] relative to the matrix. This process is followed by diffusion of metallic atoms that fill electrically active vacancies in the metallic sublattice of  $Pb_{1-x}Sn_xTe$  and  $Pb_{1-x}Sn_xSe$ .

In the present paper we report the results of an experimental study of the electrophysical properties and ESR of the  $Pb_{1-x}Ge_xTe$  ( $x=0,03$ ) doped with manganese, and of laserinduced transformations of intrinsic and impurity defects under the influence of infrared laser light.

## 2. Samples and their electrical properties

The  $Pb_{1-x}Ge_xTe:Mn$  ( $x=0,03$ ) single crystals were grown by Bridgmen technique. The Mn impurity was introduced into the melt as the MnTe compound. The impurity concentration in the melt was  $N_{Mn} = 0.5$  wt.%. The crystals had a p - type conductivity with a hole concentration  $P_{77}$  at liquid nitrogen temperature of  $(0,1\div 3)\times 10^{18} \text{ cm}^{-3}$ . The samples, cut from

the ingots, were about  $7 \times 1 \times 1,5 \text{ mm}^3$  and oriented in  $\langle 001 \rangle$  direction along their long side.

The crystals were exposed to IR light at  $h\nu < E_g$  ( $E_g$  is the width of the  $\text{Pb}_{1-x}\text{Ge}_x\text{Te}$ : Mn ( $x=0,03$ ) band gap at 300 K),  $\lambda = 10,6 \text{ }\mu\text{m}$  ( $\text{CO}_2$  – laser). The power density (W) of the laser light was below threshold at which the crystal would melt. The temperature of the samples in the course of the illumination was held well below the temperatures required for the thermal transformation of defects.

In the course of the illumination of crystals  $\text{Pb}_{1-x}\text{Ge}_x\text{Te}$ : Mn ( $x=0,03$ ) as well as  $\text{PbSnTe}$ ,  $\text{PbSnSe}$  [5-7] the density of holes decreased and an inversion of the type of conduction (Fig.1, curve 1). The time needed to cause inversion is determined by the laser radiation power density, but the rate of the changes was an order of magnitude lower than in  $\text{PbSnTe}$ ,  $\text{PbSnSe}$  (for the same treatment conditions). After the inversion of the type of conduction in contrast to  $\text{PbSnTe}$  and  $\text{PbSnSe}$  the density of electrons decreases, but their mobility is still low ( $\mu_{77} = 2 \times 10^2 \text{ cm}^2/\text{V}\cdot\text{s}$ ) while in  $\text{PbSnTe}$  and  $\text{PbSnSe}$  after inversion the electrons mobility increases and reaches the maximum value for these crystals. The temperature dependences of the Hall coefficient  $R$  (T) and resistivity  $\rho$ (T), of  $\text{Pb}_{1-x}\text{Ge}_x\text{Te}$ : Mn ( $x=0,03$ ) is shown in Fig.2 for a constant laser power density and various illumination times.

As it is shown in the figure after the inversion of the type of conduction in a temperature dependence of electrical resistivity  $\rho$ (T) at  $4,2^0 \text{ K} < T < 300^0 \text{ K}$  the sector with a pronounced minimum at  $T = 29^0 \text{ K}$  appears (fig. 2, curve 3<sup>1</sup>).

The laser - stimulated changes in the electrical properties are of a bulk nature, as can be seen from the changes in the optical transmission in accordance with the changes in the density of free carriers.

The results indicate that the mechanism for the interaction of the IR laser light with the crystal matrix is complicated and does not involve thermal processes.

It is well known that concentration supercooling in IV- VI compounds gives rise to regions enriched in the intrinsic metal and chalcogen components, and that as a result of doping these regions may acquire a wide spectrum of chemical compositions ranging from monatomic to quaternary compounds [9,10]. Inhomogeneities of this type form potential barriers with the crystal matrix. These barriers cause an intense scattering of holes at low temperatures, as can be seen in the anomalous behavior of the mobility and Hall coefficient as function of the temperature. The presence of barriers is confirmed by the strong photo-emf signals in the absence of a bias voltage. The red boundary of this emf is determined by the type of dopant. In addition, interstitial atoms, which may be electrically active, are present in a substantial conservation in the crystal.

As the IR laser light interacts with the crystal, it leads to a dissociation of regions of this type and also to a diffusion of intrinsic and impurity ions in the field of the electromagnetic wave. This process should be accompanied by an increase in the concentration of isolated manganese ions at the metal sites of  $\text{Pb}_{1-x}\text{Ge}_x\text{Te}$ : Mn ( $x=0,03$ ), which in its turn should increase the ESR signal of the impurity.

### 3. ESR spectra and discussion of results

We investigated the ESR signal using a VARIAN –E 12 system and this was done at temperature 4,2 – 300 K at the frequency  $\nu = 9 \text{ GHz}$ .

In the  $\text{Pb}_{1-x}\text{Ge}_x\text{Te}$ :Mn ( $x=0,03$ ) crystals, which were not exposed to laser radiation, the ESR spectra consisted of six isotropic hyperfine structure (HFS) lines with the half-width  $\Delta H \approx 8,6 \text{ Oe}$ , typical of isolated  $\text{Mn}^{2+}$  ions in the lattice of IV-VI crystal and due to the interaction between the  $3d^5$  electrons of  $\text{Mn}^{2+}$  with an intrinsic nuclear moment

**Laserstimulated Changes of the Physical Properties of some Solid State Solutions**

( $I=5/2$ ) of the  $^{55}\text{Mn}$  isotope (curve 1 in Fig. 3). In this case the constants of the spin Hamiltonian had the following values:  $g = 2,0005 \pm 0,0005$  and  $A = (60,2 \pm 0,2) \times 10^4 \text{ cm}^{-1}$ , where  $A$  is the hyperfine structure constant.

Interaction of laser radiation with  $\text{Pb}_{1-x}\text{Ge}_x\text{Te}:\text{Mn}$  ( $x=0,03$ ) crystals resulted eventually in an increase in the integral intensities of isolated hyperfine structure lines in the ESR spectrum (Fig.1). In addition, six auxiliary isotropic lines appeared in the ESR spectra at higher values of the magnetic field.

The intensity of each of the six lines, observed in unirradiated crystals, first rose slightly, reached saturation, and then fell (curve 3 in Fig.1); these hyperfine structure lines were not observed in the  $n$  - type conduction region. The intensities of the additional six hyperfine structure lines then increased (curve 2 in Fig.1) and near each HFS as well as  $\text{PbTe}:\text{Mn}$  [11] the satellites are appeared, caused by the superhyperfine interaction (SHFI) of  $\text{Mn}^{2+} 3d^5$  electrons with the nuclear moments of  $\text{Te}^{125}$  and  $\text{Te}^{129}$  ( $I = 1/2$ ) in the first coordination sphere a natural substance 6,67 and 0,58 % accordingly (curve 2 in Fig. 3). The constants of the spin Hamiltonian for the additional six lines were as follows:  $g = 1,9987 \pm 0,0005$ ,  $A = (60,2 \pm 0,2) \times 10^4 \text{ cm}^{-1}$ ,  $\alpha_{\text{Te}} = (15,0 \pm 0,2) \times 10^4 \text{ cm}^{-1}$ ; where  $\alpha_{\text{Te}}$  is the superhyperfine structure constant.

It should be pointed out that the half-width  $\Delta H$  of the hyperfine structure lines then decreased considerably ( $\Delta H = 5,0 \text{ Oe}$ ).

A detailed analysis of the ESR spectra showed that initially the  $\text{Mn}^{2+}$  ions occupied mainly interstices in the crystal and the appearance of the additional sextet isotropic lines and superhyperfine structure lines due to exposure to laser radiation could be attributed to the appearance of  $\text{Mn}^{2+}$  ions at lattice sites in the matrix of the  $\text{Pb}_{1-x}\text{Ge}_x\text{Te}$ :

$\text{Mn}$  ( $x=0,03$ ) crystal, which concentration increased with increasing treatment time.

The investigation of a temperatural and angle dependencies ESR spectra of solid solutions of  $\text{Pb}_{1-x}\text{Ge}_x\text{Te}:\text{Mn}$  ( $x=0,03$ ) showed that at  $T = 29^0 \text{ K}$  it appeared irregularity because of strong angle dependence in ESR spectra as well as for electrical resistivity (fig.4) and it appeared more wide lines of hyperfine interaction and also appeared temperatural dependence of HFS lines intensity (fig.5), looking like  $\rho(T)$  dependence.

It should be noted that such irregularity in exposed and not exposed crystals of  $\text{Pb}_{1-x}\text{Ge}_x\text{Te}:\text{Mn}$  ( $x=0,03$ ) with p-type conductivity not obtained. They were not obtained also at region near  $T=29^0 \text{ K}$ . It was thought that phase transition in  $\text{Pb}_{1-x}\text{Ge}_x\text{Te}$  was the transition of shifting type, but some authors [12] suppose, that unstability of lattice appears because of unstability of atoms of Ge and that is why the phase transition has type transition from regularity to unregularity.

Consequently, the anomaly in  $\rho(T)$  dependencies and also temperatural and angle dependencies of intensity of HFS lines, which was not obtained in ESR spectra of  $\text{PbTe}:\text{Mn}$  [11] and  $p\text{-Pb}_{1-x}\text{Ge}_x\text{Te}:\text{Mn}$  ( $x=0,03$ ), may be follows from redistribution of Ge between the sites of  $\text{Pb}_{1-x}\text{Ge}_x\text{Te}:\text{Mn}$  ( $x=0,03$ ) lattice and differences in dimensions of Ge and Pb. Ion radius of the Ge is approximately two times less than of Pb and that is why, when Ge takes place of Pb, the deformation field of lattice, which means that cubic symmetry changed to axial symmetry, which brings to changes of angle dependence of HFS,  $I(T)$  and  $\rho(T)$ .

**4. Conclusion**

Our investigation of the electrophysical properties and ESR of the solid solutions  $\text{Pb}_{1-x}\text{Ge}_x\text{Te}:\text{Mn}$  ( $x=0,03$ ) showed that in the charge state  $\text{Mn}^{2+}$  the Mn impurity occupies mainly interstices and also present in inactive ESR complexes. The application of the IR

laser light at ( $\hbar\omega < E_g$ ) leads to a distribution of intrinsic and impurity components (without changes in their charge state) among lattice sites and to changes in the carrier density.

Appearing at  $T = 29$  K under influence of IR laser radiation anomaly in conduction and ESR spectra connected with phase transition, which is under condition of laser stimulated distribution of Ge at lattice site and local unstability of Ge atoms.

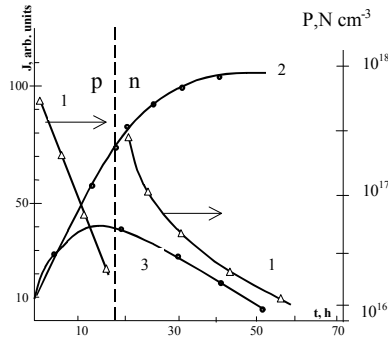


Fig.1

Fig.1. Dependencies of the free carrier concentration ( $P, N$ ) ( $T = 77$  K) and intensities ( $I$ ) of the ESR lines of  $Mn^{2+}$  in  $Pb_{1-x}Ge_xTe:Mn$  on the duration of laser irradiation: 2.-  $Mn^{2+}$  in lattice site; 3 -  $Mn^{2+}$  in interstitial position ( $W = 25$  W/cm<sup>2</sup>,  $T = 20$  K).

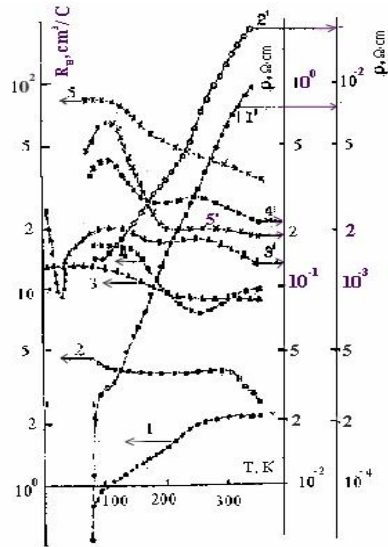


Fig.2

Fig.2. Temperature dependence of the resistance ( $\rho$ ) and Hall coefficient ( $R_H$ ) for a constant laser power density and various illumination times: (1-5) -  $R_H(T)$ , (1'-5') -  $\rho(T)$ : 1,1'- 0 h., 2,2'- 6 h., 3,3'- 26h., 4-4'- 49h., 5-5'- 60 h. ( $W = 25$  W/cm<sup>2</sup>).

## Laserstimulated Changes of the Physical Properties of some Solid State Solutions

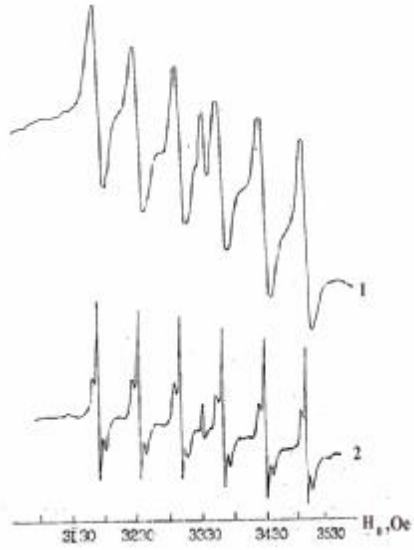


Fig. 3

Fig.3. The ESR spectrum of the  $Pb_{1-x}Ge_xTe:Mn$  ( $x=0.03$ ): 1 - before laser irradiation; 2 - after laser irradiation within 60 h. ( $T=20$  K).

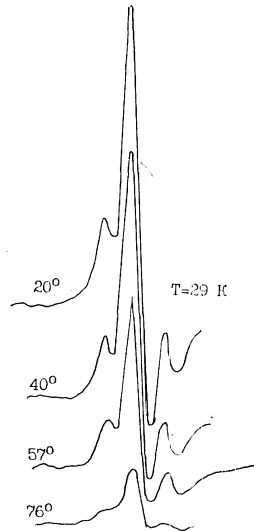


Fig. 4

Fig.4. Angular dependence of HFS lines in  $Pb_{1-x}Ge_xTe:Mn$  ( $x = 0.03$ ) ( $T = 29$  K).

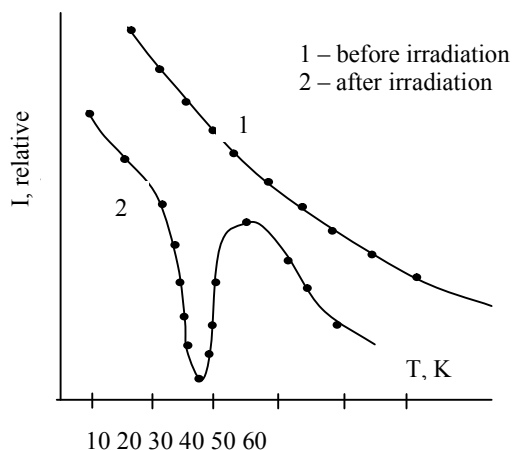


Fig. 5

Fig.5. Temperature dependence of HFS lines intensity in  $Pb_{1-x}Ge_xTe:Mn$  ( $x = 0.03$ ).

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