STRUCTURE OF PHOTOLUMINESCENCE SPECTRA OF UNDOPED GASB AND GASB DOPED BY FE

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Abstract. The modified floating-zone technique involving electric and magnetic fields allows obtaining fairly pure single crystals of undoped GaSb and GaSb doped by Fe. The structure of photoluminescence spectra of undoped GaSb is experimentally identified as radiative transitions of BE_1, BE_2, BE_3, and BE_4. In terms of a hydrogen-like model, the activation energy of impurities on which excitons are localized is calculated. The samples GaSb doped by Fe had a p-type of conductivity and it was shown that the Fe in GaSb formed the shallow acceptor level with the ionization energy of 23±2 meV. The concentration of shallow acceptors determined from the Hall measurements is in a good agreement with the concentration of the Fe acceptors obtained from the photoluminescence.

Keywords: Photoluminescence; GaSb doped by Fe; complex exciton; lifetimes; acceptor.

Introduction. Gallium antimonide, which falls into the $A^{III}B^{V}$ group of semiconductor compounds, is underresearched. Until recently, GaSb has been regarded as a material of little promise mainly due to the high concentration of intrinsic defects (~10^{17} cm^{-3}). However, the advantageous structure of energy bands and the high-impurity solubility in gallium antimonide allowed obtaining tunnel diodes and coherent-light sources. In connection with this, the interest in gallium antimonide has significantly increased in recent years. The latest data testify that the gallium antimonide narrow-bandgap semiconductor is one of the intensively studied and promising materials for designing optoelectronic devices, including thermophotovoltaic cells [1], light-emitting diodes [2], photodiodes [3], and other unusual microelectronic devices.

Despite a wealth of work done in the domain of studying the properties of gallium antimonide, still there are some problems related to the properties of this compound that have been researched insufficiently or hardly studied at all. Among these problems, there are processes of recombination and scattering of charge carriers, donor-acceptor interactions, etc. The problems of the effect of various impurities on modification of the above physical processes continue to be relevant. Photoluminescence in *p*-GaSb was studied by many authors [4, 5]. The known literature data show that the structure of radiative recombination spectra depends heavily on gallium antimonide technology. At the same time, an integrated view point with respect to identifying the structure of radiative recombination spectra is absent in the literature. The authors of [6] have developed an unusual technology for obtaining and purifying gallium antimonide single crystals. It is only natural that this gave rise to the interest

in the study of the structure of radiative spectra. In this work, we report the results of analysis of the structure of photoluminescence spectra of gallium antimonide.

Results and discussion of undoped GaSb

The gallium antimonide single crystals under study were obtained using a modified floating-zone technique. The samples exhibited the p-type conduction. The concentration (N_A-N_D) measured at 77 K varied within ($2\cdot10^{16} \div 2\cdot10^{17}$) cm^{-3}. The photoluminescence was excited by circularly polarized light of a laser with an oscillation wavelength of 1.52 μm (0.814 eV), i.e., with the quantum energy approximately equal to the band gap of gallium antimonide at 2 K, or 1.15 μm (1.078 eV). The excitation density in all the experiments did not exceed 10 $W\cdot cm^{-2}$. For these excitation levels, the concentration and the lifetimes of nonequilibrium carriers are always lower by a few orders than the intrinsic hole concentration in the samples. At temperatures of 2-4.2 K, all the valence band states above the Fermi level are occupied by holes; therefore, the effects of self-absorption and back radiation could not have a distorting effect on the form of recorded spectra. Circularly polarized light excites electrons with preferentially one orientation of spin into the conduction band. If the recombination rate of electrons does not depend on their spin, then it is obvious that the accumulation of spin-oriented carriers will take place in the conduction band. The accumulation can occur even at the excitation intensities at which the concentration of excess minority carriers (electrons of *p*-GaSb) is still low in comparison with their equilibrium concentration; as a result, radiative recombination will be polarized. The photoluminescence spectra measured at temperatures of 2-77 K are polarized. The depolarization of the photoluminescence in a transverse magnetic field (the method of optical spin-orientation of electrons, the Hanle effect) allowed determining the lifetimes of nonequilibrium carriers. It is known that the method of optical orientation of electrons makes it possible to measure extremely short lifetimes up to 10^{-11} s in conditions of continuous excitation [7].

Figure 1 depicts the photoluminescence spectra for two of the studied *p*-GaSb samples recorded at 2 K in the absence of external magnetic field (spectrum *1*for the *p*-GaSb sample with N_A-N_D = $2\cdot10^{16}$ cm^{-3}; spectrum *2* for the *p*-GaSb sample with N_A-N_D = $1.8\cdot10^{17}$ cm^{-3}; ε_g (2 K) ≅ 0.813 eV).

It is seen from the given experimental results that the photoluminescence spectra of these two samples have a fairly complex structure. As the N_A - N_D concentration increases, the photoluminescence intensity integrally decreases approximately by a factor of 1.7 in the described experiments. Using the approaches known in the literature, we shall give the identification of the experimentally observed features of the structure of photoluminescence spectra at T = 2 K in the absence of external magnetic field.

The spectrum exhibits a single energy band, which is designated with *A* in the figure, with the maximum energy $(\hbar\omega_A)_{max}$ = (777±0.2) meV and a complex band, which is integrally designated by us as the *C* band. Against this radiative band with a complex structure, features

(4-5) stand out. Replicate experiments confirm that energy band *A* represents the conduction band to acceptor (intrinsic acceptor) transitions; the complex radiative band is due to the collapse of a few exciton states. For the components of this complex band, we introduce the designations borrowed from [4].

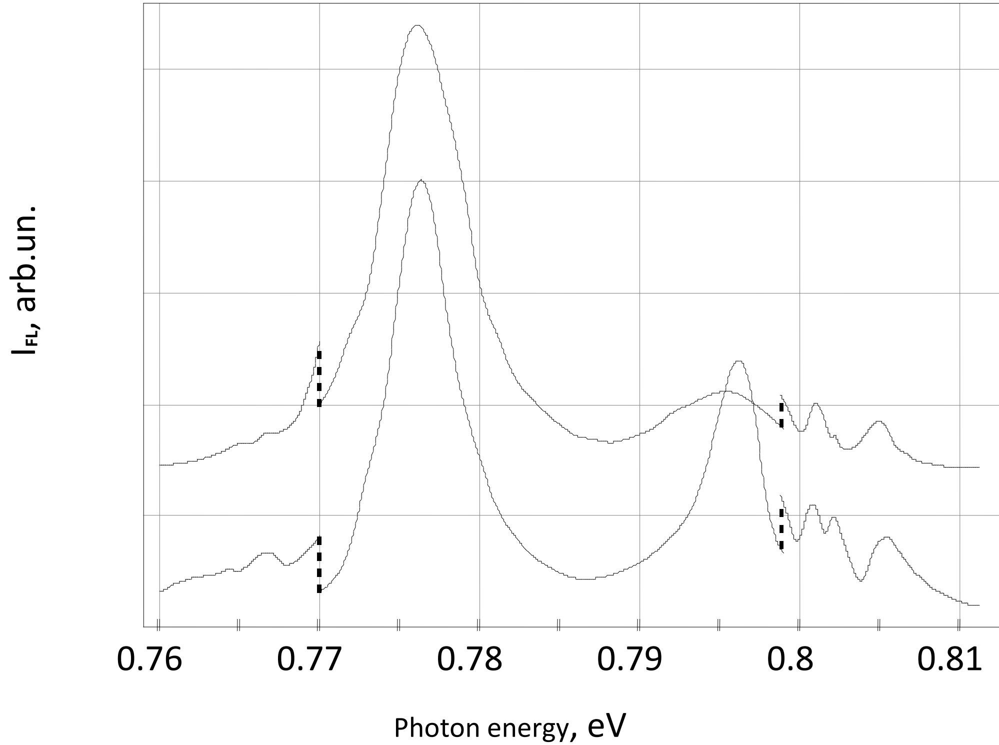

Fig.1. Photoluminescence spectra for two of the studied *p*-GaSb samples recorded at 2 K in the absence of external magnetic field (*1*- $2{\cdot}10^{16}$ cm^{-3}; 2- $1.8{\cdot}10^{17}$ cm^{-3})

Using the known Fock-Alentz technique [10], we decomposed the complex exciton band into components BE_1, BE_2, BE_3, and BE_4 (fig.2). The energy maxima of these excitons have the following values: $(\hbar\omega_1)_{max}$ = (805.2±0.2) meV (BE_1); $(\hbar\omega_2)_{max}$ = (802.3±0.2) meV (BE_2); $(\hbar\omega_3)_{max}$ = (801.1±0.2) meV (BE_3); and $(\hbar\omega_A)_{max}$ = (796.3±0.2) meV (BE_4). Knowing from the experiment the energetic position of bound excitons, in terms of a hydrogen-like model, we calculated the activation energy of respective impurity states at the following values of effective masses: m^*_e=0.041m_e for electrons and m^*_{hh} = 0.4m_e for heavy holes. For the activation energy of the impurities on which excitons are localized had the following values, respectively: ε_{A1} = 6.8 meV, ε_{A2} = 9.7 meV, ε_{A3} = 11 meV, and ε_{A4} = 16 meV. These values are in agreement with the literature data on the impurity states in gallium antimonide.

As regards the known models of spin relaxation, our calculations confirm that a significant role in gallium antimonide is played by the Bir-Aronov-Pikus mechanism [9].

In our opinion, the features of radiative recombination spectra designated in Fig. 1 through *C* and *D* are nothing else than phonon replicas of bound exciton BE_4.

The modification of radiative recombination spectra under the influence of temperature was also studied experimentally. Figure 3 shows the temperature shifts of observed exciton states. The continuous line depicts the theoretical calculation of the function $\varepsilon_g = \varepsilon_g(T)$. The shifts have the same shape; at a temperature of ~23 K exciton states collapse. At a temperature of 77 K, the BE_4 exciton band is transformed into a band corresponding to the radiative band to acceptor level transitions. As the temperature increases, these two lines are also transformed; at room temperature, one broad band corresponding to the conduction band to valence band transition remains in the spectrum

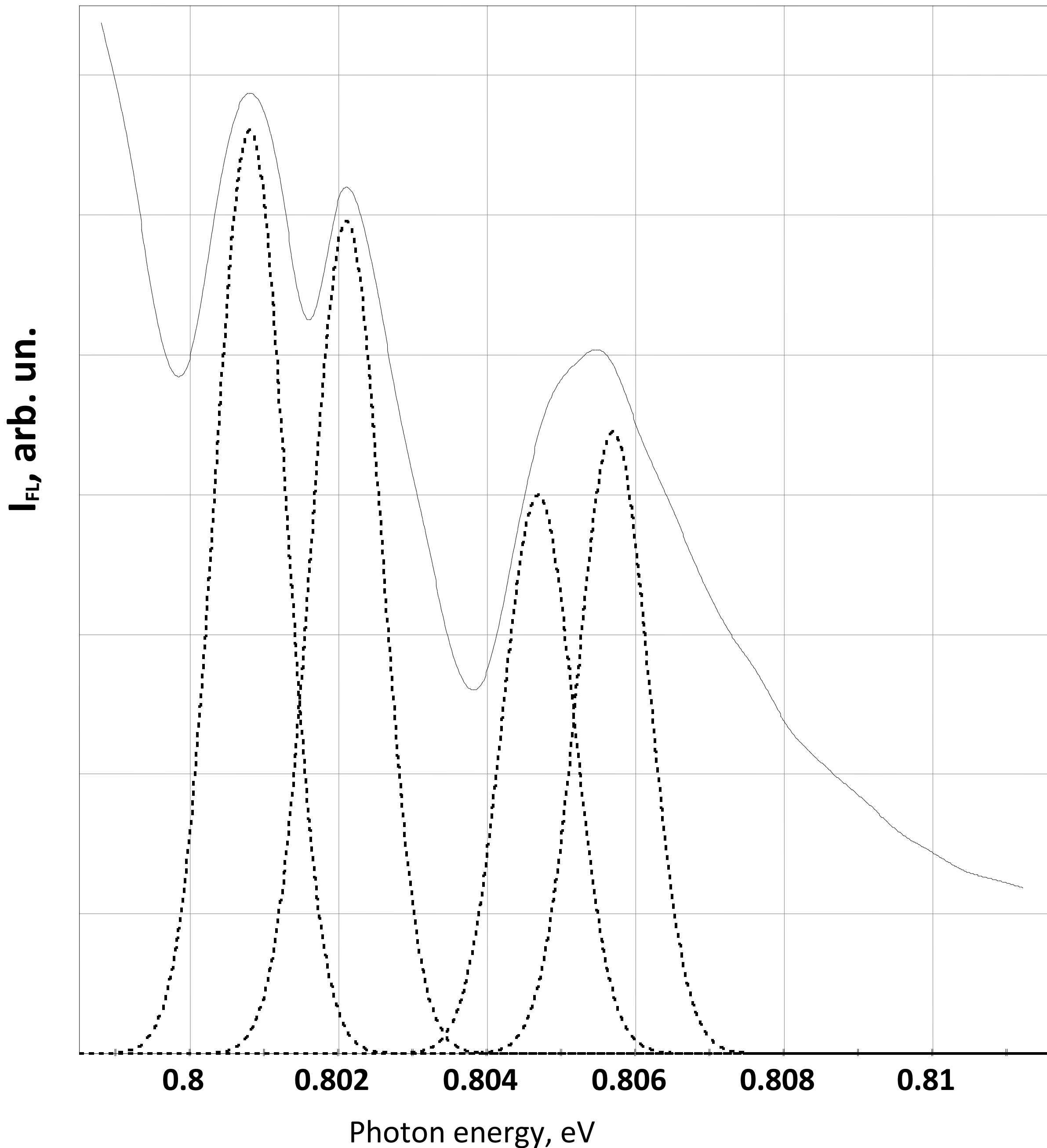

Fig.2. The photoluminescence spectra of p-GaSb and expansion exciton bands on the components BE_1, BE_2, BE_3 and BE_4.

Results and discussion of GaSb doped by Fe

The low temperature (2K) photoluminescence of gallium antimonide doped by iron have been studied at a zero magnetic field. The samples were prepared by the float-zone method. The concentration of Fe in the melt was in the range of 0.001 - 1 atomic percent. The undoped and Fe doped samples exhibited a p-type conduction. The concentration of free holes (*NA – ND*) in the undoped GaSb samples measured at room temperature varied within (2·1016 - 1.8·1017) cm-3. While, the concentration of free holes in the samples doped by Fe was in the range of (2.8·1017 – 2·1018) cm-3 and it depends on the concentration of introduced iron. The photoluminescence was excited by circularly polarized light of a laser with a wavelength of λ = 1.52 μm (0.814 eV), i.e., with the photon energy approximately equal to the band gap of gallium antimonide Eg = 0.811 eV at 2 K [12]. The excitation density in the experiments did not exceed of $10 W/cm^{-2}$. For this excitation level, the concentration of non-equilibrium carriers is lower by a few orders than the intrinsic hole concentration in the GaSb samples. At temperature of 2K, the states in the valence band up to the Fermi level are occupied by holes; therefore, the effects of self-absorption could not have a distorting effect on the form of recorded spectra. The photoluminescence spectra were measured by using a 0.75 m grating spectrometer equipped by a Ge detector. The samples were immersed into liquid helium and the temperature of 2K was obtained by pumping of helium vapor.

Circularly polarized light excites electrons with preferentially one orientation of spin into the conduction band. In direct semiconductors like GaSb, the selection rules for optical transitions from the uppermost valence band to the lowest conduction band are commonly based on the simple picture that the electron states in the conduction band have spin S=1/2 whereas the hole states in the valence band have an effective spin S=3/2 [13]. The hole states with spin z component Sz= ±3/2 are denoted heavy-hole (hh) states whereas the light-hole (lh) states have *Sz*= ±1/2. The transition probability from the hh states to the conduction band is three times larger than from the lh states. In bulk semiconductors, we thus expect that the maximum attainable degree of spin polarization is Ps=0.5, where Ps=(N+-N-)/(N++N-) and N+(N-) is the number of electrons with spin up(down) respectively. If the recombination rate of electrons does not depend on their spin, then it is obvious that the accumulation of spin-oriented carriers will take place in the conduction band. The accumulation can occur even at the excitation intensities at which the concentration of excess minority carriers (electrons of p-GaSb) is still low in comparison with their equilibrium concentration; as a result, radiative recombination will be polarized. The photoluminescence spectra measured at temperatures of 2-77 K were polarized. The depolarization of the photoluminescence in a transverse magnetic field (Hanle effect) allows determine the lifetime of nonequilibrium carriers. It is known that the method of optical orientation of electrons makes it possible to measure extremely short lifetimes up to 10^{-11}s in conditions of continuous excitation [7], (Aronov et al., 1983).

Photoluminescence spectra of the analyzed specimens are plotted in Fig 3. The spectra have been registered at T= 2K in the absence of an external magnetic field The depicted experimental results demonstrate that radiative recombination spectra at the given temperature have a complex structure and are subject to gradual modifications with increasing Fe concentration in the initial matrix. For comparison, Fig. 3 also shows the radiative recombination spectrum of the undoped GaSb measured at the same temperature, in the absence of a magnetic field. The procedure of identification of the structure of the spectrum of the undoped GaSb is described in [12]. Below we present an analysis of the radiative recombination spectrum of the undoped GaSb registered at T=2 K, in the absence of a magnetic field. In Fig.3, spectrum 1 was registered for a specimen of p-GaSb with N_A-N_D=2·10^{16} cm^{-3} (E_g(2K)=0.813 eV). The test results indicate that the radiative recombination spectrum of the undoped specimen has a number of clearly pronounced energy structures. Fig.3 shows as well a simple energy band denoted by the authors as A, with the energy max $(\hbar\omega_A)_{max}$=77±0.2meV and a complex band integrally denoted as B. Four to five features stand against the background of an energy band with the complex structure.

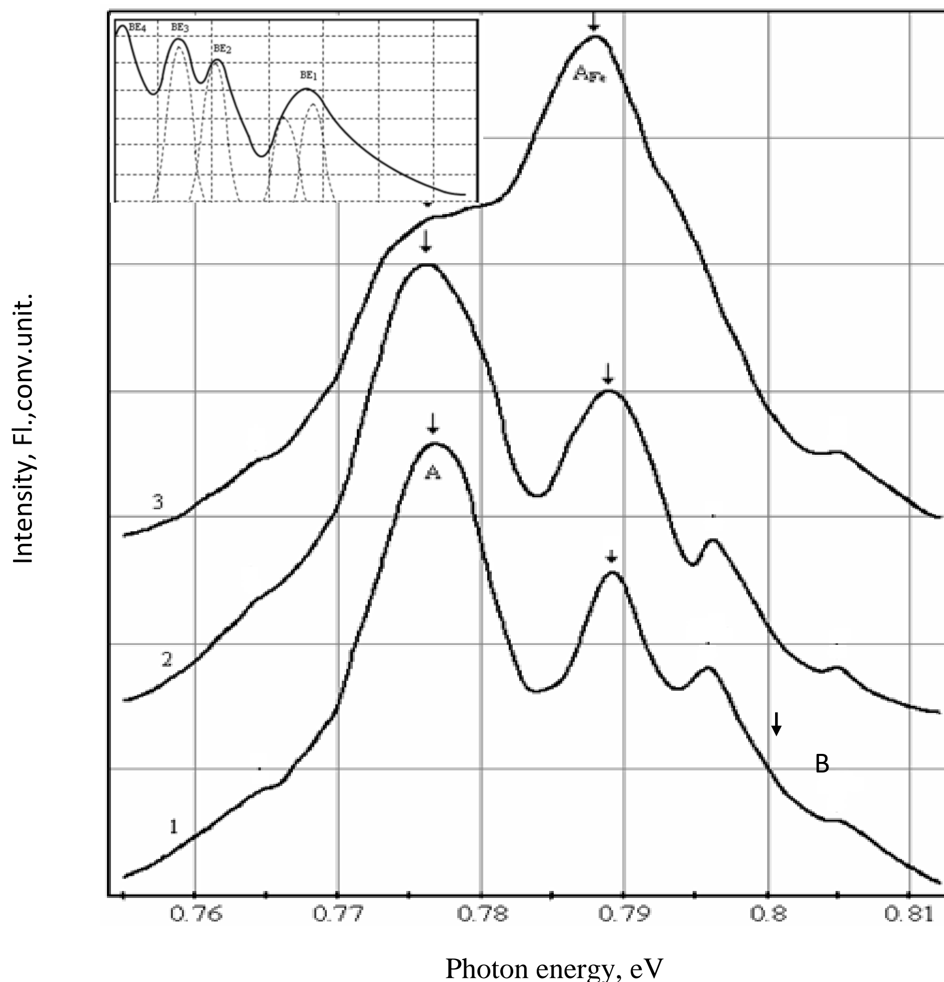

Fig. 3. Radiative spectra of Fe-doped GaSb at T = 2 K, B = 0. The interser is unfolded presenteation of B segment of spectra.

$1.\ GaSb\langle Fe\rangle,\quad 0{,}000\ \%\quad Fe,\quad N_A - N_D = 2{,}0\cdot 10^{17}\ cm^{-3}$
$2.\ GaSb\langle Fe\rangle,\quad 0{,}010\ \%\quad Fe,\quad N_A - N_D = 2{,}8\cdot 10^{17}\quad cm^{-3}$
$3.\ GaSb\langle Fe\rangle,\quad 1{,}000\ \%\quad Fe,\quad N_A - N_D = 1{,}8\cdot 10^{18}\quad cm^{-3}$

Additional tests confirm that the energy band A registres donor-acceptor recombinations. Taking into account the literature data stating that the energy of the activation of donor levels in GaSb is 2÷3 meV, the energy of the activation of acceptor levels was established by the authors of the present paper as being E_i=34±0.2 meV. This result is in conformity with our findings on the same specimen in terms of the Hall constant and electrical conductivity..

Spectrum 2 in Fig. 3 depicts radiative recombination of Fe-doped GaSb at T= 2K, in the absence of an external magnetic field. The concentration of the incorporated Fe is minimal – 0.001 % atomic percent. Spectrum 2 as well as Spectrum 1 of the radiative recombination of Fe-doped GaSb has a complex structure. The analysis of the former spectrum allowed to conclude the following. In the main, the general structure of spectrum 2 is analogous to the structure of the radiative spectrum of the undoped specimen: the energy state of band A is preserved, the radiation intensity does not change. However, there is the two-fold attenuation of the intensity of radiation of the block of bands identified as bound excitons, and a negligible shift in the high energy region of the exciton maxima BE_1, BE_2, и BE_3. Between the exciton block B and the radiation band A (with the participation of intrinsic acceptors) there appears a new radiation band denoted by the authors of the present paper as A_{FE}. The energy maximum of this new band is $(\hbar\omega_{A_{FE}})_{\max} = (788 \pm 0{,}2)\, meV$. The comparison of bands A and A_{Fe} demonstrates that although they have different intensity, their half-width is about the same and their dependence on the excitation intensity is really the same. These findings lead to the conclusion that those two radiative bands are of the same physical nature. The energy shift of the maximul of band A_{Fe} against the maximum of band A in the high energy region of 11±0.2 meV determines the difference in the energy of ionization of the incorporated acceptor levels and the intrinsic acceptor level, the value of the latter was established by the authors of the present paper as ε_i=35±0.2 meV. From those values of ionization energy conditioned by Fe in acceptor levels we get $\varepsilon_i(Fe) = (22 \pm 0{,}2)\, meV$. It means that the radiative band under discussion here is due to the donor-acceptor recombination.

In Fig. 3 spectra 1, 2, and 3 correspond to GaSb doped with Fe in different concentrations. Concentrations of Fe are: for spectrum 1 $(0{,}000\ \%,\ N_A - N_D = 2{,}0\cdot 10^{17}\ cm^{-3})$, for spectrum 2 $(0{,}010\ \%,\ N_A - N_D = 2{,}8\cdot 10^{17}\ cm^{-3})$, for spectrum 3 $(1{,}000\ \%,\ N_A - N_D = 1{,}8\cdot 10^{18}\ cm^{-3})$. The analysis of the obtained results reveals that the higher the concentration of Fe incorporated in the melt, the higher the intensity of the radiative band A_{Fe}, the growth being almost proportional to Fe content in an active state. In addition, the structure of the exciton module is being modified, the intensity of bands BE_1, BE_2, BE_3 is getting lower. At the concentration of the incorporated Fe of 1%, all exciton bands are bound, and in the structure of the radiative

spectrum, the dominant band is A_{Fe}, with a small shift in the high energy region, which is most probably related to the increase of N_A-N_D because of doping.

The lifetimes of nonequilibrium electrons in the specimens analyzed were established by the polarization properties of band A_{Fe}, through registrarion of the Hanle effects. Optical orientation of carriers, depolarization of luminescence in a transverse magnetic field. These findings evidence that the higher the content of Fe in the main matrix, and the higher the concentration of acceptor states, the shorter are the lifetimes of minority cariers. The observed shortening of the lifetimes of nonequilibrium electrons is nearly inversely proportional to the increase of the concentration of holes, hence being caused by the increase of the concentration of Fe in the electrically active state. From the experiment one we obtained the lifetimes of nonequilibrium electrons and, using the formula $N_t = (\tau \cdot B)^{-1}$, we established the concentration of the recombined centers. In calculations of the coeeficients of radiative recombinations, the autors used the value $B = 8 \cdot 10^{-10}\ cm^3 s^{-1}$, typical for hydrogen-like shallow centres [14]. Therefore, the effect of Fe in GaSb on the velosity of radiative recombination of carriers consists in the raise of concentration of shallow acceptor levels, and in accordance with [15], but unlike other compounds of group $A^{III}B^{V}$, does not lead to the creation of channels of a rapid nonradiative recombination. Similar conclusions were drawn in [16] for GaSb doped with Mn, the difference being the following: when doping with Mn, at the incresase of the concentration N_A-N_D (because of the higher Mn content in GaSb‹Mn›), the concentration changes about 24 times, whereas the lifetime reduces 8-fold. In GaSb‹Fe›, the concentration changes about 130 times, whereas the lifetime reduces by 58 times. The findings under discussion refer only to the study of the energy structure of the incorporated impurity centers and their influence on the recombination of minority carriers. Thus attention was not attracted to the interaction of carriers and magnetic moments that were shown for the impurities of transition metals; besides, the effect of the clusters formed on the energy structure of the main matrix was not discussed either. Still, the issues not covered in the present paper are of interest and do deserve attention in further studies.

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ANALIZA VULNERABILITĂȚII DE SECURITATE A REȚELELOR INFORMAȚIONALE

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Abstract. Vulnerabilitatea este o slăbiciune a sistemului care permite o acțiune neautorizată. Acestea sunt erori care apar în diferite faze aale dezvoltării, respective folosirii sistemelor informaționale.

Key words. vulnerabilitate, sistemul informational, rețea de calculatoare.

Introducere

Problemele de securitate din orice tip de reţea de calculatoare provine dintr-o contradicţie fundamentală a Internetului şi anume caracterul public dorit de utilizatori pentru orice resursă informaţională şi nevoia de securizare a informaţiilor şi a reţelei în sine faţă de atacurile persoanelor rău-intenţionate care urmăresc compromiterea, preluarea, modificarea sau distrugerea informaţiilor ori întreruperea funcţionării reţelei.

Datorită dezvoltării tehnologiei, sistemul informatic a devenit un instrument de comunicare indispensabil. Dar orice mijloc de comunicare, mai ales când mediul de comunicare este un mediu nesigur, cum este Internetul, prezintă riscuri. Utilizarea sistemelor informatice conectate la Internet în domenii diferite precum domeniul militar sau domeniul comercial face ca acest risc să crească.

Sistemele informaționale s-au demonstrat vulnerabile în fața atacurilor de pe Internet, la accesările neautorizate a sistemului, la modificări sau distrugeri de informații, accidentale sau intenționate. Atenuarea și corectarea acestor vulnerabilități a devenit o obligație atît pentru instituții cît și pentru persoanele fizice pentru protejarea informațiilor.