Photoluminescent investigations of SHF-irradiation effect on defect states in GaAs:Sn(Te) and InP crystals

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ABSTRACT

Results of investigations of magnetron and hyrotron irradiations effects on spectra of local states to be formed by intrinsic and impurity point structure defects in nearsurface layers of GaAs:Sn (111), GaAs:Sn (100), GaAs:Te (111) and InP (100) have been studied and discussed. The effect of SHF irradiation on defect states in GaAs and InP has been obtained to depend on both the type of dopped impurity and the orientation of sample surface. The important role of intrinsic vacancies in processes of rebuilding point and complex defects in nearsurface layers has been established. The gettering action of SHF-irradiation on point defects and the increase of homogeneity of SHF-irradiated crystals have been found. The mechanisms of SHF-fields and semiconductor compounds interactions are discussed.

Keywords: III-V semiconductor compounds, SHF-irradiation, luminescence, structure defect.

I. INTRODUCTION

One of a necessary technological operation in process of semiconductor devices production is known to be the heat treatment of semiconductors and heterostructures on their basis. At present the laser and electron beam annealings are used besides usual heat treatments. However, these methods have a number of principle difficulties, in particular, connected with homogeneousness of treatment all over big area (∅50-100 mm) and volume of material, and others. A new annealing method, using electromagnetic field of super high frequency (SHF)-irradiation, which have no mentioned difficulties has been proposed in [1].

In present work the results of investigation of magnetron (M, $f=10^{10}$ Hz, P = 100 W/sm^2, t_{irr}^{M} = 2, 6, 14, 30, 62 s) and hyrotron (G, $f = 10^{11}$ Hz, P = 10 kW/sm^2, t_{irr}^{G} = 1, 2, 3, 4, 10, 20, 30, 40 s) irradiation effects on spectra of local states to be formed by intrinsic and impurity point structure defects in such substrate materials as GaAs:Sn(111), GaAs:Sn (100) ($n=5\cdot10^{16}$ - $2\cdot10^{17}$ cm^{-3}), GaAs:Te(111) ($n=7\cdot10^{16}$- $5\cdot10^{17}$ cm^{-3}) and InP(100) ($n=2$ - $3\cdot10^{17}$ cm^{-3}), which are used for production of SHF electronic devices, have been studied and discussed.

Preliminary experiments have been shown [2] that the short time (5 s) M-treatment of Schottky diodes, which were obtained by evaporation of metals on GaAs surface, leads to improvement of some electrophysical parameters of surface barrier structures, in particular, to increase of minority carriers diffusion length. The latest is conditioned by defect states within subsurface layer of semiconductor. The aim of this work is to investigate the effect of SHF-irradiation on rebuilding of structure defects in mantioned above substrate materials by photoluminescence (PL) analysis. The PL measurements are carried out at 77 K within spectral range of 0,6 ÷ 2,5 μ. Excitation of PL was realized by light of power incandescent lamp PJ-100 with $\lambda_{ex} \leq 600$ nm.

2. EXPERIMENTAL RESULTS

Fig. 1-5 present both the PL spectra of GaAs:Sn (111), GaAs:Sn (100), GaAs:Te (100) and InP (111) single crystal wafers and changes of PL bands parameters (locations of maxima in energy scale $h\nu_m$, values of both halfwidths H and intensities in maxima W) with increasing of M- and G-irradiation times ($t_{irr}^{M,G}$).

All of initial GaAs:Sn crystals have two overlapping bands in their PL spectra: shortwave band 1 and longwave band 2, their $h\nu_m^{1,2}$ and intensities ratio W_1/W_2 depending on orientation of sample surface - fig. 1. GaAs:Te (111) crystals have a single PL band with $h\nu_m$= 1.20 eV - fig. 4. Three PL bands are observed in PL spectra of InP (100) with $h\nu_m$ = 1.4 1 eV, 1.15 eV and 0.82 eV - fig. 5.

GaAs:Sn (111). These crystals are distinguished by greater spread in $h\nu_m^1$ values than other studied crystals. According $h\nu_m^1$ values and behaviours after M- and G-irradiations we succeed in these crystals dividing into three groups with $h\nu_m$ = 1.150 eV, 1.200 eV and 1.185 eV respectively. Values of $h\nu_m^2$ are 0.993 ÷ 1.010 eV for different samples. Initial crystals have the band 1 with the intensity of 2 ÷ 5 times greater than intensity of band 2. The halfwidth of band 1 is greater one of band 2 also (H_1 = 200 ÷ 230 meV, H_2 = 100 - 150 meV at 77 K).

SHF irradiation affects on band 1 parameters more powerfully than on band 2 ones. After shortest $t_{irr}^{M,G}$ used in this work ($t_{irr}^{M,G} \leq 10s$) $h\nu_m$ values of both bands became the identical ones for all GaAs:Sn (111) crystals studied and they are $h\nu_m^1$ = 1.185 eV, $h\nu_m^2$ = 1,010 eV. Just these $h\nu_m^{1,2}$ values are observed at initial crystals of 3[d] group. Change of $h\nu_m^1$ occurs abruptly and is accompanied by abrupt decreasings of both intensity and halfwidth of band 1 - fig. 1,a.

When t_{irr}^M is increased, intensities of band 1 in crystals of 1[t] and 2[d] groups are slightly increased, the bands 1 is become narrower, while parameters of bands 2 do not change practically. M- irradiation do not effect on parameters of both bands in crystals of 3[d] group (fig. 2,e).

G-irradiation effects on band 1 parameters by different manner for crystals of different groups: it decreases the intensity of band 1 in crystals of group 1 and increases thats in crystals of group 2 and 3 - fig. 2, b, d, f. Regimes t_{irr}^G = 40 s for crystals of group 1 and t_{irr}^G = 10 s and 20 s for crystals of group 2 are seemed to be separated ones: apparently, at these regimes the crystals were overheated because of in observal form they acquired red colour during irradiation. Values of $h\nu_m^{1,2}$ are changed abruptly up to 1.28 eV and 1.04 eV respectively. At the same time, the band 1 intensity is decreased, and that of band 2 are increased, so that the band 2 is become more intensive than band 2. The same manner (sharply) halfwidths of bands are changed also - fig. 2, b, d.

GaAs:Sn (100). In these crystals two overlapping bands are observed too, however the longwave band 2 with $h\nu_m^2$ = 0.996 ÷ 1.002 eV is the more intensive one - fig. 1, d. The shortwave band 1 positions are 1.220 ÷ 1.240 eV in different samples.

At short $t_{irr}^{M,G}$ (up to $t_{irr}^M \leq 30$ s, $I_{irr}^G \leq 4$ s) $h\nu_m^{1,2}$ are appeared to be the same ones for different samples and to work out $h\nu_m^1$=1.240 eV and $h\nu_m^2$=1.010 eV. The band 2 intensity at t_{irr}^M = 2 s is decreased sharply and then slightly increased as t_{irr}^M is rised - fig. 3,a.

At $t_{irr}^{M,G}$ = 60 s and t_{irr}^G >10 s, $h\nu_m^1$=1.280 eV as for "overheated" samples of GaAs:Sn (111). At short t_{irr}^G < 10 s the intensities of band 1 an 2 are changed in opposite manner: the band 1 is increased, but the band 2 is decreased (fig. 3, b). Thus, in G-irradiated GaAs:Sn (100) crystals intensity of band 1 becames greater than ones of band 2 - reverse situation in comparison with "overheated" GaAs:Sn (111) crystals, which have the same $h\nu_m^{1,2}$.

In GaAs:Te (111) M-irradiation does not practically effect on $h\nu_m$ and halfwidth of 1.200 eV band, while it's intensity is increased, when t_{irr}^M is rised - fig. 4. G-irradiation do not effect on the shape of PL band also, its intensity being changed unmonotonous manner: up to t_{irr}^G = 10 s that is increased and then decreased up to initial values at t_{irr}^G = 40 s.

InP (100). SHF -irradiation of InP (100) by both M- and G-generators over 1 s to 40 s do notchange $h\nu_m$ of all bands observed, the 1.150 eV band loses its structure, the intensity of band 1.410 eV is slightly decreased at short

t_{irr}^{M} and then increased. The rest of bands intensities are increased also, but the weaker than band 1.410 eV one - fig. 5.

3. DISCUSSION

The results obtained testify the initial impurity-defect states of GaAs nearsurface layers are defined by both type of doped impurity and orientation of sample great side as well as by uncontrolled impurities, which may contaminate on the crystal surface when it is treated (e.g. from etchant). Besides, one must take into account that own mechanical stresses, which are arised in GaAs waters when the monocrystals are subjected to cutting out and to further chemical-machanical treatment, may effect on defect composition of nearsurface layers, depleting or enriching of thats with vacancies.

According to literature data, centres of band 1 in GaAs:Sn with $h\nu_m^1 = 1.150 \div 1.220$ eV are donor-axcceptor (DA) complexes (V_{Ga} + Sn_{Ga}) (see, for example [3]), but of band 2 - isolated acceptors Cu_{Ga} [3]. Our experimental data, in particular, relative narrowness of band 2 in comparison with band 1 are not at variance with these assumptions.

Spread in values of $h\nu_m^{1,2}$ to be observed by different authors and by us within lot of initial samples may be caused by possible different separation (r_{AD}) between D and A in mentioned complexes in lattice, as well by D and/or A nonequivalent positions in lattice due to prescence in theirs environments other (different) defects, local own mechanical stresses, dislocation, etc. The whole of mentioned facts cause the so-called inhomogenous broadening of PL bands.

Different ratio of bands 1 and 2 intensities in GaAs:Sn samples which are cutted out from the same single crystal ingot and subjected to the same chemical-mechanical treatments, but having different crystal orientation of wafer great side, may be connected with the greater concentration of V_{Ga} into surface layers of GaAs (111) crystal than (100) one. Crystals of A^3B^5 compounds are known to have anisotropy of energy properties. Basic crystallographic planes in GaAs have different free surface energies [4]: $\sigma_{100}>\sigma_{110}>\sigma_{111}$, here σ_{hkl}-specific surface energy. Thus, one may think that the plane with the lesser surface energy will have the more concentration of intrinsic defects - vacancies.

Simultaneous and abrupt changes of both $h\nu_m^1$ and H_1 in GaAs:Sn (111) at very short t_{irr}^{M} testify to both introducing some order into latice and homogenization of r_{AD} within complexes up to the same values in different samples caused by SHF-actions. The most stable DA complexes have been obtained to be the centres of band with $h\nu_m^1$=1.185 eV. It will be recalled that just that $h\nu_m^1$ value was observed in PL spectra of 3^d group's samples, PL parameters of which do not change up to the most M-expositions t_{irr}^{M} = 60 s - fig. 3, a. Apparently the GaAs:Sn (111) of 3^d group were the most perfect (homogeneous) between all of GaAs (111) ones studied in work.

Selectivity of M-irradiation effect on band 1 in GaAS:Sn (111) crystals indicate to the canal of nonradiative recombination is not affected, when lattice is ordered at used regims of SHF-irradiation, because of in the opposite case the intensities of both bands should have changed by the same manner ($\sum_i R_i = 1$ at the same PL excitation conditions before and after SHF-action, R_i - the part of carriers flow through i-canal radiative and nonradiative recombination [5]. Just that behaviour was observed in GaAs:Sn (111) crystals of 3^d group at G-irradiation (fig. 3.b). That indicates on weakening of nonradiative recombination canal in these crystals at that treatment. When t_{irr}^{M} rises, some (weak) rise of band 1 intensity in GaAs:Sn (111) crystals of 1^t and 2^d groups is apparently caused by that M-irradiation either stimulates the rise of V_{Ga} concentration in nearsurface layers of these crystals, or promotes the more intensive process of complex formation from available Sn_{Ga} and V_{Ga} by means of taking away the obstacles (another defects) on the way of their unification (lattice ordering). We think that the first way is the more preferable one due to of if the second way was realized, we should observe the transformation some PL band, connected with V_{Ga}, into 1.185 eV band, that in experiment do not observe.

The experiments confirm that the band 2 is connected with uncontrolled isolated Cu impurity in GaAs:Sn (111): M-irradiation do not effect on its parameters practically.

In crystals GaAs:Sn (100), the band with $h\nu_m^1$ = 1.24 eV is observed. According 3, centres of this band are Sn_{As} - acceptors. At t_{irr}^{M} = 60 s and t_{irr}^{G} = 10 s concentration of V_{As} rises and complex formation from available Cu_{Ga} and arising V_{As} is taken place. (Cu_{Ga} + V_{As}) complexes are known to be centres of 1.28 eV band [3]. The fact of complex formation at mentioned regimes of irradiation is confirmed by proportional changes of band 1 and band 2 intensities - fig. 5,b.

In GaAs:Te (111) the emission centres of a single 1.200 eV band are (V_{Ga} + Te_{Ga}) complexes [3] to be stable ones: neither M-, nor G-irradiations effect on a shape of this band. The changes of its intensity with $t_{irr}^{M,G}$ increasing are apparently determined by irradiation effect on centres of nonradiative recombination.

Literature data have no definite interpretation about nature of 1.41 eV band in InP. In some work this band is connected with uncontrolled presence of Si-impurity [3], in others - with V_P [3] or with band-to-band recombination of nonegilibrium carriers [3]. Asymmetric band in the region of 1.06 ÷1.15 eV with phonon structure is caused by (Fe_{In} + V_P) complexes [3]. Relative narrowness of 1.41 eV band in comparison with 1.15 eV band allows to prefere V_P as centre of the former band. The rise of both bands intensities after M- and G-irradiation indicates to possible V_p concentration increase, which form the band 1.41 eV centres and are the component of 1.15 eV band centres. So far as the isolated V_P acceptors have the most cross section of nonegillibrium holes capture than DA complexes [5], the rise of V_P concentration must effect more effective on band 1.41 eV intensity. That is observed in experiment.

4. CONCLUSION

Thus, the effect of SHF-irradiation on defect structure of nearsurface layers and on processes of rebuilding of centres of radiative recombination in GaAs and InP has been obtained to take place and to depend on both the type of dopped impurity and the orientation of sample surface. The important role of vacances in defect centres rebuidings in GaAs nearsurface layers in wafers with different orientation of samples great side has been established. The natures of centres of PL bands studied have been defined more exactly. The facts of bands narrowings and obtained identical values of PL band $h\nu_m$ in irradiated crystals are assumed to be connected with the increase of homogeneity of irradiated crystals, possible due to local heating processes of heterogeneities.

To ascertain the micromechanisms of interaction of SHF-irradiation with semiconductor compounds and heterostructure on their basis, the further experiments are needed, which are in progress.

5. REFERENCES

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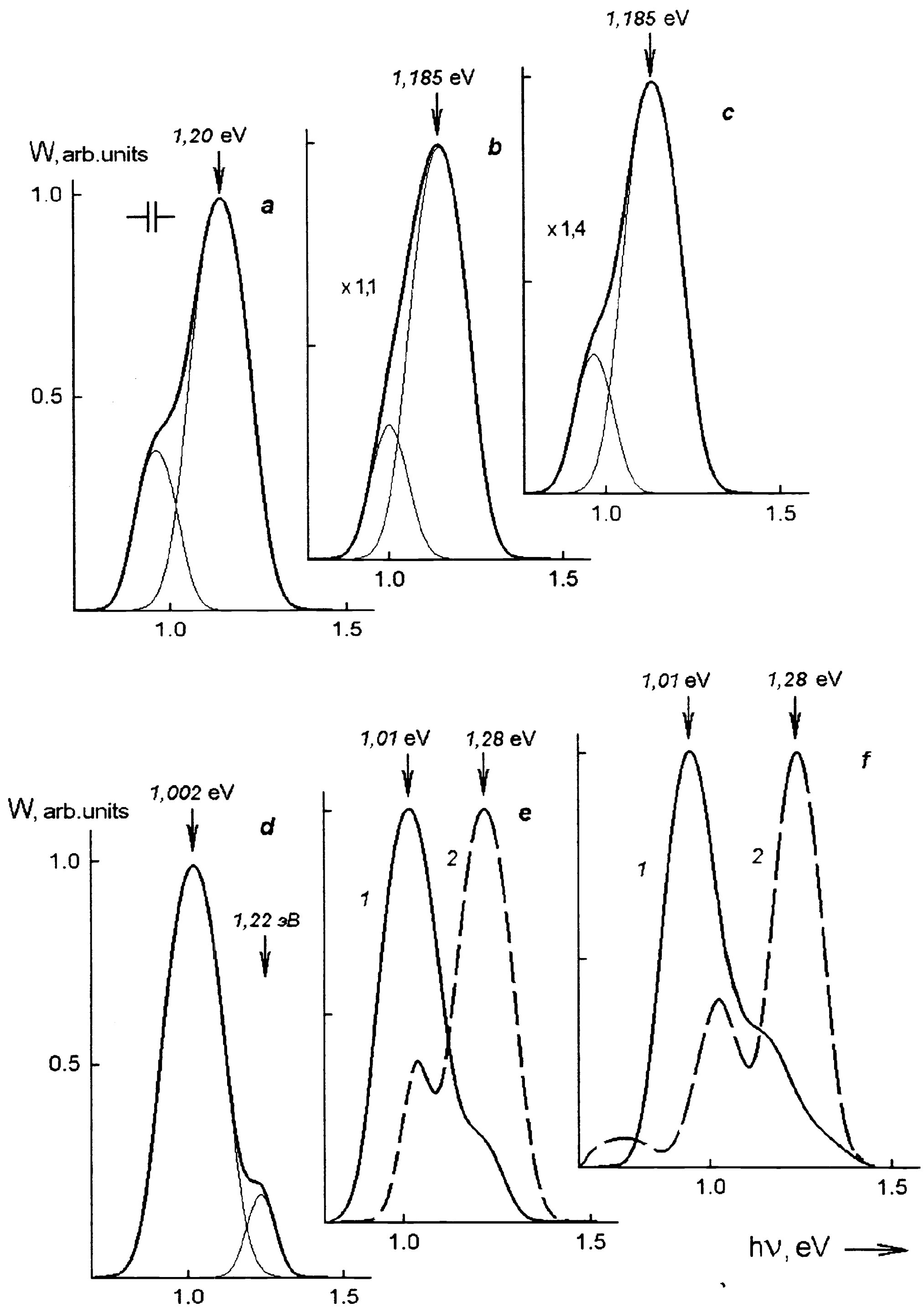

Fig. 1. PL spectra of GaAs:Sn (111) (2^d group sample) (a-c) and GaAs:Sn(100) (d-f) before (a,d) and after irradiation by magnetron (b, c) at t^G_{irr} = 10 s (b), 60 s (c) and gyrotron (e,f) at t^G_{irr} = 1 s (e,1), 10 s (e,2), 4 s (f,1), 40 s (f,2) generators. T=77 K.

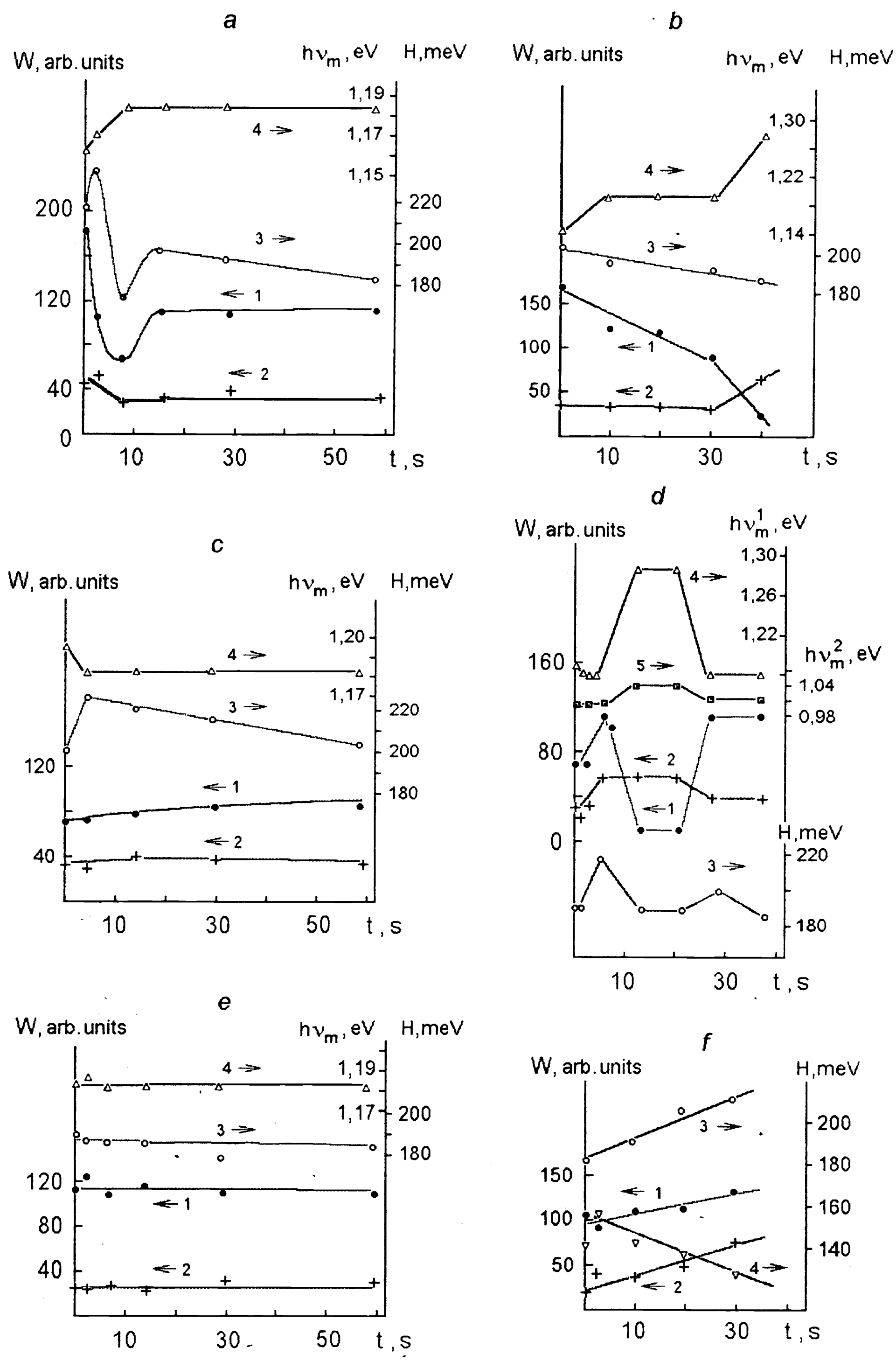

Fig 2. Dependences of intensities of bands 1 (curves 1) and 2 (curves 2), halfwidth of band 1 (curves 3), maxima positions of band 1 (curves 4) and band 2 (curve 5) on irradiation times of GaAs:Sn(111) samples of groups 1 (a, b), 2 (c,d) and 3 (e, f) by magnetron (a, c, e) and gyrotron (b, d, f) generators.

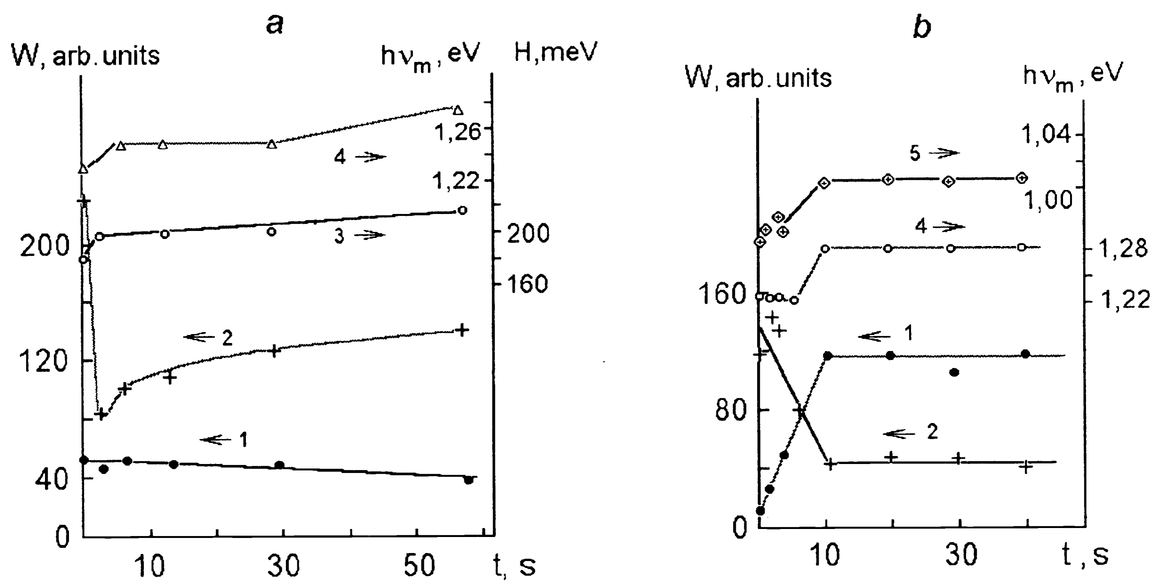

Fig. 3. Dependences of intensities of bands: 1 (curves 1), 2 (curves 2), halfwidth of band 1 (curves 3), maxima positions of bands: 1 (curves 4), 2 (curve 5) of GaAs:Sn(100) on irradiation times of magnetron (a) and gyrotron (b) generators. T = 77 K.

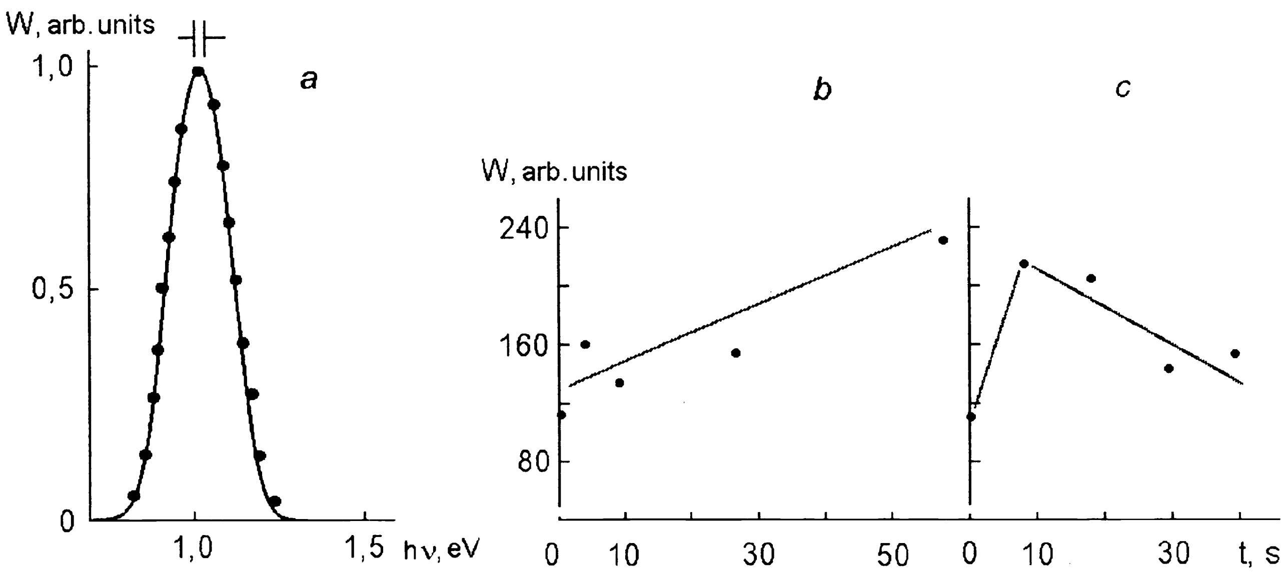

Fig.4. PL spectra of GaAs:Te(100) (a) and dependences of band intensity on irradiation times of magnetron (b) and gyrotron (c) generators. On (a) solid line - for initial crystal, points - after G-irradiation at t^G_{irr} = 40 s. T = 77 K.

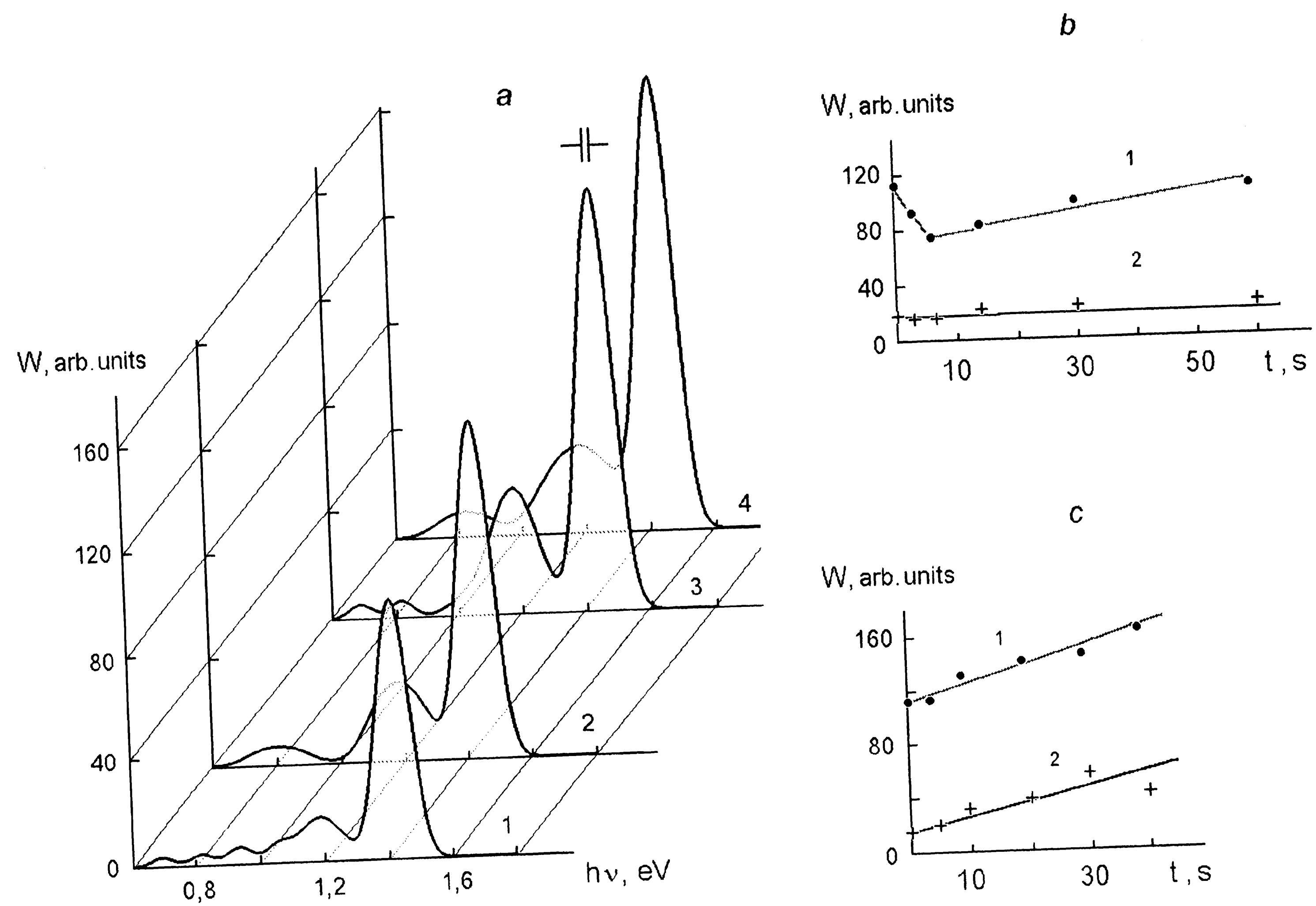

Fig. 5. PL spectra of InP(111) crystal (a) before treatment (1), after G-irradiations at t^{G}_{irr} = 10 s (2), 30 s (3), 40 s (4) and dependences of intensities of band 1,41 eV (curves 1) and 1,15 eV (curves 2) on irradiation times of magnetron (b) and gyrotron (c) generators. T = 77 K.