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Defect reorganization induced by pulsed magnetic field in porous InP

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Abstract. We present results of investigations of the effect caused by weak magnetic field (B = 60 mT) in porous InP crystals of impurity-defect composition. This effect was found when studying the spectra of radiative recombination within the range 0.6 to 2.0 μm at 77 K. It was obtained that field influence initiates long-term changes in the intensity of radiative recombination inherent to centers of different nature. A possible mechanism of observed transformation is discussed.

Keywords: photoluminescence, weak magnetic field, impurity-defect composition.

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1. Introduction

Great attention to obtaining and researching self-organized semiconductor layers of low dimensions based on III-V single crystals arose in recent years. It is possible to relate to their number porous materials created by arrays of long channels with a submicrometer cross-section that appear during anode etching of semiconductor by halogenous electrolytes. Due to qualitatively new properties that are absent in bulk materials, the possibility to use single crystal substrate with known parameters and simplicity of technology for porous structure formation in the reason for wide interest to these objects. Besides, in recent years porous layers were applied in technology to obtain epitaxial layers with good structural perfection. For example in [1], it has been shown that use a porous substrate gives InP epitaxial layers with a low number of elastic strains and low concentration of dislocations. Therefore, search of new technological methods to influence on the structure of porous materials is now very topical. Pulsed magnetic field (MF) treatment is the more perspective and cost-effective one. Influence of this field on the electron spin localized on defect in semiconductor results in changes of mechanical and electro-physical properties [2].

At the same time, researching defect reorganization caused by MF treatment of III-V semiconductors has not been developed yet. There are no experimental results indicative of interrelation processes between microstructure of defects and efficiency of the reaction conditioned by treatment in weak MF.

Thus, to ascertain the nature of MF phenomena in semiconductor crystals, on the one hand, researches carried out at MF treatment of defect structure using spectroscopic methods and, on the other hand, the objects with different structural states are required. In this case, porous structures are more interesting due to its formation occurring in irreversible, non-linear processes and very non-equilibrium thermodynamic conditions, but its microcrystalline structure has much wider surface area, than that of bulk material.

2. Experimental

The defect structure of the samples was studied using the photoluminescence (PL) method at 77 K in the spectral range 0.5…2.0 eV. Excitation of PL was realized using light of a powerful lamp with $h\nu > 2.0$ eV. The absorption coefficient of investigated semiconductor in this spectral range was $\sim 10^5\ \mathrm{cm}^{-1}$. Thus, the spectrum of defects was studied within the subsurface layers with the depth close to $\sim 10^{-5}$ cm. Porous structures prepared in accord with the technique described in [1] on low-resistivity n-type indium phosphide with the surface orientation (100) and concentration of carriers close to $2\times 10^{18}\ \mathrm{cm}^{-3}$ was the object of our investigations.

3. Results and discussion

Atomic force microscopy (AFM) images of por-InP samples, which confirmed a different level of structural homogeneity in the prepared objects, are shown in Fig. 1.

After the cause of etching that lasted more than 25 s, the layers with a higher density of pores making a regular network were obtained (Fig. 1a). The optical measurements of reflectivity were carried out at 300 K within the spectral range of 950 to 1100 nm and resulted in interference image. The latter was formed by two interfering optical beams: reflected from surface of the porous layer and from porous layer-substrate interface. This fact testifies about the high level of phase homogeneity in the above layers.

To ascertain features of recombination processes in porous structures and possibility of influence of the pore surface, we consider changes in parameters of PL bands with time after treatment in MF ($B = 60$ mT, $f = 10$ Hz, $t = 60$ s) in more details (Fig. 2).

PL spectra of our samples in their initial state consist of only two bands – at 1.15 and 0.9 eV. The band-to-band radiative recombination at 1.41 eV (at 77 K) was not observed. Perhaps, due to absorption of this emission in porous sublayer bulk and re-radiation via the localized levels of pore surface [1]. If the density of localized states is sufficiently large, it results in narrowing of por-InP band gap and in red band shift. The band in the region of 1.15 eV is caused by complexes of native point defects. X-ray photoelectron spectroscopy experimental data confirm it [1]. It was obtained that the sample surface and bulk of the porous layer are passivated by products of electrochemical oxidation, i.e. in this case reduction of the surface state density could be found.

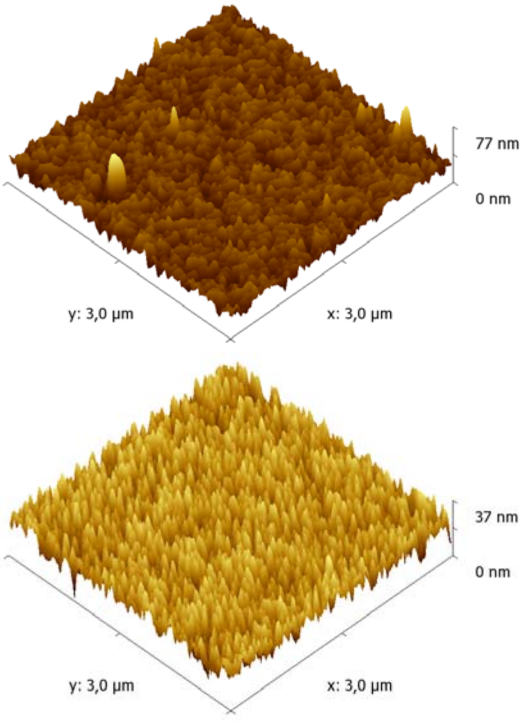

Fig. 1. Different microrelief of porous material.

On the other hand, electrochemical etching results in infringement of stoichiometry of the initial crystal and enrichment of near-surface layer by P vacancies. The latter can form associative pairs with impurities and other defects, which results in appearance of impurity bands: with $h\nu^1_{\max} = 1.15\,\text{eV}$ and wide with a lower intensity at $h\nu^2_{\max} = 0.9\,\text{eV}$. According to [3], we should believe that the second band is related with donor-antisite defect P_{In}. But for large concentration of P_{In}, deviation of the InP sample stoichiometry toward an excess of metalloid is required, which is in contradiction with the results of electrochemical etching. However, if we consider a presence in the composition of the In oxide passivated layer, then appearance of the antisite defect like P_{In} in small concentrations can be found probably. The latter results in appearance of the band with low intensity related with this defect. This is in good agreement with our experimental data.

The MF treatment resulted in essential increase in the intensity of the band at 1.15 eV. The intensity of the second band increases, too, but much less than the latter one. The frequency positions of PL peaks do not vary. The intensity of the band with $h\nu^1_{\max} = 1.15\,\text{eV}$ decreases down to the initial value after some time interval (several days), but for the second peak it does not vary. Much longer time delay (up to 7 days) results in increase of the intensity of both bands.

Thus, the phenomena of short-term effect of MF treatment on porous InP structures resulted in long-term non-monotonous changes in its PL intensity was found. One can ask about a reason of observable changes. Popular believe held that the intensity of PL increases, while the concentration of non-radiative centers decreases, and vice versa. Absence of the edge band is indicative of a high concentration of these defects. But the questions about non-monotonous, long-term changes in the PL intensity of observable bands and role of MF in these phenomena are still open.

According to [4], MF treatment of SiO_2-Si structures results in relaxation of internal mechanical strains, which possesses non-monotonic view. It should be noted that the strains of squeezing of near-surface layer were transformed to strains of tension but then returned to initial ones. The relaxation process starts at treatment and proceeds during several days. It is accompanied by changes in the thickness of oxide layer: at first, it decreases, but then it becomes larger.

There is a high concentration of strain and broken bonds in near-surface layers of spatially-nonhomogeneous porous structures. So, we consider that the above phenomena take place in our case, too. The most probable mechanism of MF influencing on semiconductor material is as follows. Strained chemical bonds are weakened due to magnetic-induced intercombination transitions of electrons that take part in formation of these bonds. On the other hand, the polarization of nucleus magnetic isotopes (^{31}P, spin $I = \frac{1}{2}$), when electrons change their spin orientation due to nuclear relaxation and pass to antibonding states [5], can results in this weakening. The destruction of weakened chemical bonds due to thermal fluctuation and mechanical strains is accompanied by appearance of mobile charged point defects and amplification of oxidation processes. It should be noted that the peak of pulsed MF effect (increase in the oxide layer thickness) was reached in 5 to 6 days after treatment [6]. Oxidation of the surface results in its passivation (decrease of surface electron levels density), i.e. in the decrease of radiationless recombination. The increase in PL intensity after 8-days delay in our case can appear due to such process.

It should be emphasized that the presence of native mechanical strains and their relaxation can result in reorganization of defects in semiconductor, too. In the work [7], authors have observationally proved the necessity of the account of deformation effects when observing reorganization of local centers in GaAs interface. According to [8], the presence of elastic strains causes the change in the chemical potential of point defects as compared with that of non-deformed crystals. The direct diffusion flux of these defects appears due to this circumstance. The state of vacancies supersaturation is realized at the strains of squeezing presence. This supersaturation relaxes to new equilibrium state of the system due to the flow of vacancies and dislocations to surface region, or/and to creation of complexes and clusters of point defects. If the strains of tension are present, we deal with destruction of these complexes and clusters that consist of vacancies. The level of supersaturation or undersaturation by vacancies depends on the concentration of doped and background impurities, which can take part in formation of the impurity-vacancy complexes – the centers of radiative and nonradiative recombination. The observed features of reorganization in the impurity-defect structure in conditions of changing the strain “sign” of semiconductor state after MF treatment [4] can result in the change of spectral allocation of radiation. I.e., it can result in the increase or decrease in the PL intensity of impurity bands, as it was obtained in [7] where correlation of the strain “sign” in the semiconductor structures with the changes in PL spectra was obtained.

Processes of the association of defects in complexes and the dissociation of the lasts at room temperature are slowed due to a low value of the diffusion factors of native and impurity defects. It can be the reason of the observed long-term changes in PL spectra.

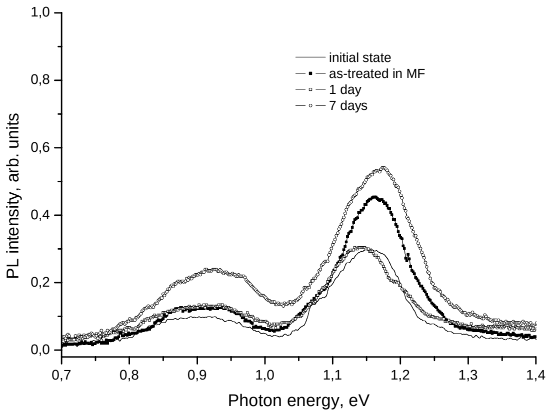

Fig. 2. PL spectra of porous InP of the first group (Fig. 1a).

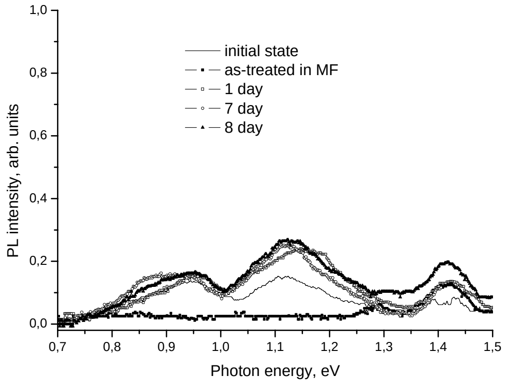

Fig. 3. PL spectra of porous InP of the second group (Fig. 1b).

The spectral dependences of the reflectivity in the structures with morphology shown in Fig. 1 were similar to those of bulk material. However, the value of reflectivity for porous layer was smaller than that for bulk semiconductor. The latter is caused, perhaps, by the increase of the contribution of diffusion dissipation in these objects. As to these samples, the differences in PL spectra were obtained (Fig. 3).

The weak edge emission at $h\nu_{\max}^{\text{edge}} = 1.41\,\text{eV}$ in these samples, at difference from previous structures, has been observed. A big half-width of this band testifies about its not-simplicity. Probably, it has been created by bands with different but close maximums. The wide impurity bands testify about large chemical and spatial non-regularities of centers corresponding to observed emission. The treatment in MF results in quenching all the observed impurity bands, but edge and new at $h\nu_{\max}^{3} = 1.3\,\text{eV}$ ones appear. The latter is related, perhaps, with radiative recombination caused by continuum of surface levels, situated below the conduction band that resulted in red shift of edge peak. Long-term changes in PL spectra similar to those in the first group were obtained.

4. Conclusion

The results of our structural, photoluminescence and optical investigations of the nanostructured InP have demonstrated a qualitative similarity of reorganization of defect structure for both groups of semiconductor caused by MF that are in good agreement with noted conception. Some differences in spectra of radiative recombination can be explained by deviation in impurity-defect composition of initial substrate, morphology of porous layers, value of internal mechanical strains and oxide processes.

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