BOUND EXCITONS IN LONG-TIME ORDERED GaP:N

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The results of investigations of long-time ordering of nitrogen atoms along P sites in 35 years ago grown GaP single crystals and related phenomena in N impurity-bound excitons are presented. It was shown that during this period impurity redistribution due to the respective substitution reaction with the energetic barrier 1.0-1.2 eV at room temperature and normal pressure leads to regular distribution of N along anion sites. A combine molecular beam and laser assisted method of growth of GaP thin epitaxial films periodically doped with N atoms is proposed. Possible properties of high density bound excitons in these epitaxial films have been discussed taking into account that the ordered N impurity-bound exciton phase of high density gives new opportunities for appearance of various non-linear optic phenomena, accumulation, conversion and transport of light energy.

INTRODUCTION

It is known that Gallium Phosphide (GaP) is highly prospective both for various applications (photoreceivers, light emitters, electroluminescent displays, power diodes etc.) as well as a model material for investigations of fundamental properties of semiconductors. In particular, GaP doped with nitrogen N or GaP:N is a unique object for generation, investigation and application of bound exciton system which is mostly interesting in the field of high density of excitons bound to ordered N-impurity superlattice. Due to considerable efforts in single crystal growth during my graduate and postgraduate courses (1963-1966) at State Technical University, A.F. Ioffe Physico-Technical Institute (St.Petersburg, Russia) and Moldavian Ac. Scie. Institute of Applied Physics now, probably, only I am the owner of the unique collection of over 35 years “matured” single crystals of pure and doped Gallium Phosphide. It seems that very interesting long-time changes periodically for years observed in these crystals give a unique opportunity to develop new generation of electronic devices as well as physics of ordered excitonic state.

The main goals of the paper are (i) to discuss the results of investigations of long-term ordering of nitrogen atoms along P sites in 35 years ago grown GaP single crystals and related phenomena in N impurity-bound excitons, (ii) to propose the methods of growth of GaP thin epitaxial films periodically doped with N atoms and (iii) to discuss their possible application.

RESULTS AND DISCUSSION

The single crystals were grown in 1963-1966 at very steep cooling of diluted melted solution of pure P in Ga with a small quantity of GaN [1]. Parameters and properties of the noted above GaP crystals such as temperature dependences of conductivity and Hall effect, photoconductivity and luminescence at various temperatures and levels of optical excitation were investigated in the years of their preparation as well as during the years after. The mostly considerable results obtained for these years are the development of growth technology for perfect and free of contamination doped crystals, investigation of influence of crystallization conditions on morphology and quality of crystals [1], discovering of impact ionization of bound excitons [2], stimulated emission of radiation through indirect optical transition [3], “giant” shift of luminescent bands in dependence on intensity of exciting light and increase of quantum output of irradiation [4, 5], multi-quantum optical transitions with participation of 2 - 7 photons or 2 photons and a phonon participation in an elementary light absorption act [6, 7], collective properties in high density bound exciton system [8] as well as long-

time ordering (LTO phenomenon) of impurities and host elements in these crystals for 35 years aged at normal conditions [9-12].

N impurity-bound excitons in GaP:N are under investigation around the world since early 60th [13, 14]. Luminescent spectra of excitons and excitonic molecules bound to isolated N atoms ($\mathbf{r_{NN}} > 5$ nm, where $\mathbf{r_{NN}}$ - the average spacings between N impurities), as well as excitons bound to NN pairs ($\mathbf{r_{NN}}$ = 1.2 nm and less) have been investigated to the middle of 70th. Main properties of bound excitons of high density {$(\mathbf{n_1} \times \mathbf{a_1}^3)^{1/3} \cong 1$, where $\mathbf{n_1}$ and $\mathbf{a_1}$ - bound exciton concentration and Bohr radius respectively, $\mathbf{a_1}$ = 5 nm, $\mathbf{n_1} = \mathbf{N_0} \cong 10^{18}$ cm^{-3}} have been also studied [8, 15, 16]. These investigations show that all groups of luminescent particles such as free excitons, excitons and excitonic molecules bound to single N atoms, excitons bound to NN pairs have their own specific luminescent spectra consisting of zero phonon line and its phonon replica. One can select experimental conditions in which only one group of particles gives the main contribution to luminescence. However, due to a stochastic distribution of impurities inside the crystals each of the groups is present and can be experimentally distinguished.

For the first time it was shown that the system of high density bound excitons can be considered as a solid excitonic phase like an inverted alkali metal and consisting of a net of negatively charged heavy nuclei (N atom + captured electron) which interacts with a free hole gas [8]. Since electrons are being captured by a short-range potential of impurity states while holes are being bound by a long-range Coulomb interaction, N isoelectronic impurities localize electrons much stronger than holes. Thus, creation of this phase was recognized by specific changes of luminescence spectrum at high density of bound excitons (Fig. 1) as well as by p-type photoconductivity of highly optically excited GaP:N in photo-Hall measurements compared to always n-type dark conductivity of these crystals (Fig.2) [8, 9, 12].

It was also demonstrated that in spite of random distribution of N impurities along P sites just after preparation of GaP:N crystals, disposition of impurities only in anion sites as well as intense Auger recombination between the bound excitons disposed at a too short distance to each other ($<a_1$) give some initial ordering of the dense excitonic phase.

In 1980 M.Combescot and C.B. a la Guillaume [16] have made a theoretical generalization of the experimentally observed collective properties published for the first time in 1974 by S.L.Pyshkin and L.Zv. Zifudin [8]. The authors [16] have proved that there exist two successive phase separations for an electron-hole system in a semiconductor having isoelectronic impurities within a certain density range. One is between bound excitons and a hole plasma with electrons pinned on the impurities, and the other one is between this hole plasma and the usual electron-hole plasma.

Thus, 25 years ago a solid excitonic phase with some inclinations of ordering like an excitonic crystal has been predicted and discovered. In contrast to the high density system of free excitons admitting only liquid phase and not existing in solid state, the solid bound excitonic phase has heavy nuclei with small zero vibrations like an usual crystal with metallic bonds, rather high critical temperature destroying this new phase (21 meV) and the lifetime 10^{-7} s [17] which is enough to observe its creation.

A new stage of experiments with the aged (grown in the middle of 60th) GaP:N crystals has started at the beginning of 90-th when a dramatic evolution of their luminescent and Raman spectra (Figs. 3 and 4) has been revealed.

1. Very intense in fresh crystals doped by 10^{19} cm^{-3} and more of N (average $\mathbf{r_{NN}}$ = 3 -5 nm) NN_1 - NN_{10} luminescence of excitons bound to NN pairs with the spacing $\mathbf{r_{NN}}$ from 0.345 nm (NN_1) to 1.219 nm (NN_{10}) is completely absent in the same crystals 25 years after their growth. This experimental result means that the degree of impurity ordering in the aged crystals is rather high compared to the fresh ones - now divergences from the average $\mathbf{r_{NN}}$ do not exceed 10% in the crystals doped by 4 x10^{19} cm^{-3} against 100% and more in the fresh crystals. Instead of the NN_1 -NN_{10} lines, the luminescence spectra of ordered crystals develop a broad uniform band the maximum of which shifts to the low energy region as the nitrogen concentration increases.

2. Zero phonon line A and its phonon replica of single N impurity-bound excitons in the aged crystals shift their positions with the concentration of N impurities according to the relation between of A position and N_0 concentration:

$$\mathbf{E_{NN}} = \mathbf{E_N} - \boldsymbol{\beta} \mathbf{r_{NN}}^{-3} \quad (1),$$

where $\mathbf{E_N}$ is the A line position at $\mathbf{r_{NN}} \rightarrow \infty$, $\mathbf{E_{NN}}$ is the same at some non-zero nitrogen concentration and $\boldsymbol{\beta}$ = 13 if $\mathbf{E_N}$, $\mathbf{E_{NN}}$ are measured in eV and $\mathbf{r_{NN}}$ in Å [10]. Meanwhile, compared with the ordered Ga:N the fresh crystals demonstrate only broadening of the lines when the nitrogen concentration increases that also confirms ordered disposition of impurities with equal spacing r_{NN} in the aged crystals (Fig.3). An increase of N concentration in ordered GaP:N system leads also to increase, for instance, of LO lattice phonon energy because nitrogen replaces 2 times heavier phosphorus in ordered N superlattice (Fig.4).

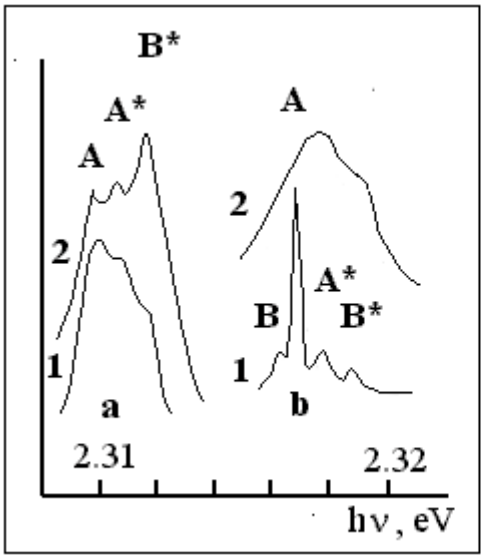

Fig. 1. Evolution of GaP:N luminescence spectra at $(\mathbf{n_1} \times \mathbf{a_1}^3)^{1/3}$ less than (1) or equal to 1 (2). a. 4.2K. b. 80K. A,B - excitons; A*,B* - biexcitons.

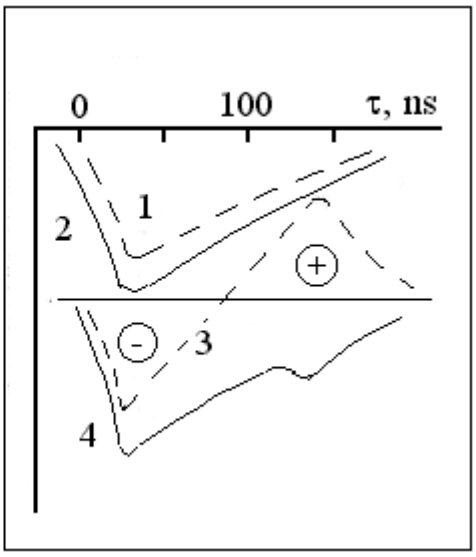

Fig.2. Kinetics of photoconductivity (solid) and photo-Hall effect (dotted) in GaP:N. . 80K. $(\mathbf{n_1} \times \mathbf{a_1}^3)^{1/3}$ less than 1 (1, 2) or equal to 1 (3,4).

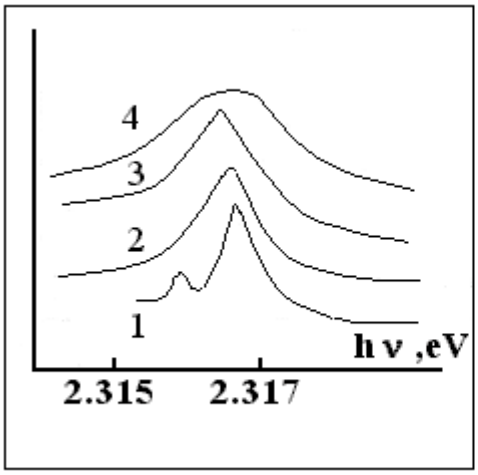

Fig. 3. Evolution of the non-phonon line of bound exciton A as a function of N concentration.15K.
1-3: ordered crystals. 4: unordered.
1-4: $\mathbf{N_o}$ = 10^{17}; 10^{18}; 10^{19} and 10^{18} N in cubic cm respectively.

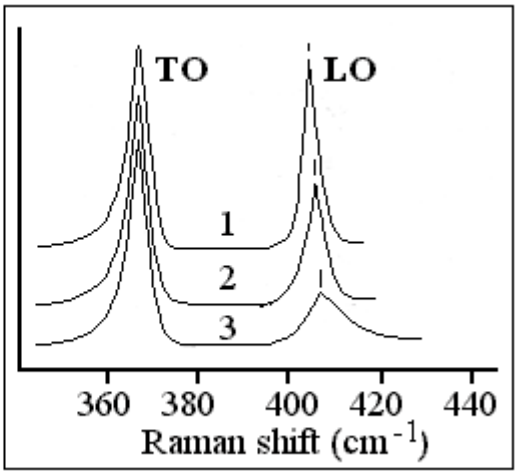

Fig.4. Evolution of LO lattice phonon energy with N concentration in ordered GaP:N according to Raman scattering at 300K. Excitation by Ar^+-laser at 514 nm. Concentration of N grows in 3 orders from 1 to 3 (app. 10^{19} N in cubic cm).

3. All the details of luminescent spectra of N impurity-bound single excitons can be observed in the aged crystals more clearly than in fresh ones. It concerns a very low background of the exciton lines as well as to their small halfwidth and distinct position in the spectrum. Thus, the observed long-term ordering is actual also for host constituents of crystal lattice. In general, GaP:N crystals are considerably more perfect after 25 years than just after their growth. Note, that nearly the same results were obtained by us for $CdIn_2S_4$, which during this period turned their partly inverse spinel structure T_d^2 into the normal spinel O_h^7 [10, 11].

Thus, it was shown that the impurity redistribution since the middle of 60-th up to the beginning of 90-th due to the respective substitution reaction with the energetic barrier 1.0-1.2 eV at room temperature and normal pressure gives regular disposition of N along anion sites.

A solid bound exciton phase is absolutely new phenomenon. Previous results [8, 9, 12] only give arguments for its existence without a proper investigation of its properties such as crystal structure, luminescence, conductivity and charge transport, non-linear effects etc. Meanwhile, it is clear that these investigations will be very interesting and useful for various applications. Particularly, if in atoms the characteristic parameter for a non-linearity appearance is the first ionization potential of the order of 10eV, the same critical parameter for an exciton crystal, the energy of exciton, is 3 order less or 10^{-2} eV only that gives an unique opportunity to generate various non-linear optical effects at very low exciting light intensity. This excitonic phase of high density gives also new opportunities for accumulation, conversion and transport of light energy. Now we plan to apply for growth and monitoring of ordered GaP:N films new growth technique, such as combined molecular beam and laser vacuum epitaxies (MBE and LVE) with various modern *in situ* and *ex situ* diagnostics of growing film [18-22] and use of in-built ion lithography. The properties of these films will be investigated in comparison with bulk ordered GaP:N crystals.

New stage in solving of the problem of crystal state of bound excitons depends on the opportunities, which give modern methods of thin film preparation and their doping by impurities.

Really, with the recent progress in film growth there is no necessity to wait an ordering for decades. For instance, superlattice from GaP/GaP:N with the period of the order of the Bohr radius, which is equal to 5 nm, can be prepared by MBE or in combination with the Laser Vacuum Epitaxy [18]. Preparation of two-dimensional net of N impurities along pure GaP film is rather difficult, but it is also possible with the help of ion lithography or atomic force microscope (AFM) built into a growth chamber. Of course, nowadays this technique is a frontier of our technological possibilities, but during the nearest 2-3 years very important results will be obtained also in this direction.

CONCLUSION

For years, properties of bound excitons were not so attractive and understandable as properties of free excitons. It seems, however, excitons (single, pairs, excitonic molecules) bound to N impurity superlattice after their proper investigations will be important object for solid-state physics and its applications in the nearest future. Especially it concerns collective properties of high density bound excitons, excitonic molecules as well as phase excitonic transitions in ordered GaP:N system. Except initial theoretical generalization and a set of experimental data in this field to the recent moment there is not any complete picture of the observed phenomena.

Both the investigation and further application of the long-term ordering (LTO) are of great interest because besides the fundamental scientific reasons the phenomenon gives a unique opportunity to considerably improve perfection of artificially grown crystals as well as to develop new or increase known useful properties applicable for semiconductor device making, probably, for watch and jeweler industries.

In particular, the ordered high density bound exciton system with app. Bohr radius distance between the excitons is a crystalline excitonic phase having unique highly useful properties. It is obvious also that wares fabricated from the aged crystals are considerably more tolerant to degradation than their fresh analogues. It was shown by us also that long-term ordering in some cases could be replaced by a short-time temperature treatment of fresh crystals.

Results of investigation of the discussed phenomena obtained with the unique collection of ordered GaP single crystals will give a new approach to fabrication of integral circuitries for opto- and microelectronics: it will concern choice of aged crystals having very stable parameters in time (low degradation of devices on their base) instead of just grown as well as realization of giant light capacity and low threshold non-linear effects in dense ordered bound excitonic phase. GaP films periodically doped by N atoms can be artificially grown by molecular beam and/or laser assisted epitaxy and will be used in new generation of mesoscopic light emitters, transducers and receivers.

This paper is devoted to 75th Anniversary of my brilliant supervisor, permanent co-author and kind adviser during of decades of my life, late academician *Sergei Ivanovich Radautsan*. The main results of the paper recently were presented among the invited talks at The 103rd Annual Meeting of The American Ceramic Society, Symposium A2: “Optoelectronic Materials and Technology in the Information Age”, April 2001, Indianapolis, USA [23].

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Charge Transfer Excitons. The lowest CT exciton state in the ab plane of an anthracene crystal with two inequivalent molecules per unit cell; the plus and minus signs refer to the center of gravity of charge distribution. The Frenkel exciton obtains when both (+) and (â€“) occupy essentially the same molecular site. 6. Crystalline Organic Films. Charged carrier mobility increases with increased. Ï€âˆ¹Ï€ ORBITAL OVERLAP. Good carrier mobility in the stacking direction. An exciton is a bound state of an electron and an electron hole which are attracted to each other by the electrostatic Coulomb force. It is an electrically neutral quasiparticle that exists in insulators, semiconductors and some liquids. The exciton is regarded as an elementary excitation of condensed matter that can transport energy without transporting net electric charge. S. L. Pyshkin Bound excitons in long-time ordered GaP:N. [pdf]. 14. Solid State Device Physics. top. M. Mereuta, S. Bouchoule, I. Sagnes, F. Alexandre, G. Le Roux, H.Sik, J. Decobert, A. Ougazzaden InGa(N)As/GaAs QW laser structures grown by MOVPE. [pdf]. 20. G.Korotcenkov, A.Cerneavschi, V.Brinzari, A.Palagnuk, A.Cornet, J.Morante, A.Cabot, J.Arbiol Ozone sensing properties of In2O3 films deposited by spray pyrolysis. [pdf]. 24.Â N.I. Leporda, A.D. Grozav Long glass-coated semimetallic and semiconducting wires prepared by two different liquid phase methods. [pdf]. 74.