GaP: Long-Term Evolution of Properties and New Prospects for Optoelectronics

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***Abstract* — A unique set of GaP semiconductor samples studied for over 50 years has exhibited significant improvement in their properties through the formation of the perfect host crystal lattice and the N-impurity crystal superlattice. This article reviews this evolution of properties and discusses their novel utility in advanced optoelectronic devices. More specifically, nitrogen-doped gallium phosphide (GaP:N) crystals that were originally prepared in the 1960s were theorized to form an excitonic crystal (1970s), and the best methods of their bulk, film, and nanoparticle crystal growth have subsequently been developed. The excitonic crystals yield novel and useful properties including enhanced stimulated emission and very bright and broadband luminescence at room temperature, which have been observed. These results provide a new approach to the selection and preparation of "perfect" materials for optoelectronics and offer a unique opportunity to realize a new form of solid-state host – the excitonic crystal – as a high-intensity light source with low thresholds for nonlinear optical effects.**

***Index Terms* — long-term evolution of crystal properties, excitonic crystal, crystals close to ideal.**

I. INTRODUCTION

Described herein are studies initiated by one of the authors (SLP) in 1961. Further studies on the same samples were conducted in the later 1960s through 1970s, then again in the 1980s, 1990s, and 2000s making these a very unique set of semi-centennial observations [1-5].

One of the most important findings of this study was the observation, first recognized in the 1980s, of a significant improvement over time in the properties of GaP crystals under atoms improved over time as did the GaP mechanical properties, luminescence with tunable spectral characteristics, and nonlinear optical effects, not observable in the freshly prepared (imperfect) crystals.

Over time, as confirmed by 50 years of experiments on the same samples, driving forces, such as diffusion along concentration gradients, strain relaxation associated with clustering, and minimization of the free energy associated with properly directed chemical bonds between host atoms, results in an ordered redistribution of impurities and host atoms in the crystal. In the particular case of GaP, as well as other compounds possessing highly volatile components, direct attempt to accelerate these processes through annealing at increased temperatures as a rule cannot be successful due to the potential for thermal decomposition (in GaP – due to P desorption).

Accordingly, successful thermal processing of these compounds can only take place at temperatures below the sublimation temperatures of their volatile constituents, requiring a longer annealing time. For instance, as evaluated in the framework of the Ising model, the characteristic time of the substitution reaction during N diffusion along P sites in GaP:N crystals at room temperature constitutes 15-20 years [2]. Hence, the observations of highly excited luminescence and some other phenomena in the crystals made in the 1960-1970s and in the 1980-1990s were then compared with the results obtained in 2005-2014 under similar experimental conditions.

The long-term ordering of doped GaP and other semiconductors has been observed as an important accompanying process, which only can be studied using the same unique set of samples and decade time scales. Jointly with Refs [1-5], this review provides a short generalization of the results on these long-term observations of luminescence, absorption, Raman light scattering, and microhardness of the bulk single crystals in comparison with the same properties of the high-quality GaP nanocrystals. It is shown that the combination of these characterization techniques elucidates the evolution of these crystals over the course of many decades. It also clarifies the ordered state brought about by prolonged room-temperature thermal annealing, and the useful optical properties that accompany such ordering. It is demonstrated that long-term natural stimuli that improve the perfection of crystals prevail over other processes and can lead to novel heterogeneous device systems and new semiconductor devices with high temporal stability.

II. EVOLUTION OF THE PROPERTIES OF GALLIUM PHOSPHIDE WITH TIME

A. Bulk perfect crystals

The method to grow gallium phosphide crystals from GaP solution melt was chosen due to the significant temperature reduction of the process and the presence of large amounts of solvent which dramatically reduce impurities from the container. Note that lamellar crystals grown from this solution melt are the most convenient and

economical material in the manufacture of many semiconductor devices.

The influence of the following factors on the quality of the grown single crystals has been investigated:

(1) quantity and chemical nature of impurities;

(2) geometric shape of the container and conditions of heat rejection;

(3) accuracy of the temperature control; and

(4) cooling rate and the law of heat-sink cooling.

The first crystals, having the form of dendritic needles with the length of the order of 5 mm and thickness of 0.15 mm, were grown at the temperature of 1107 °C, which is approximately 16 °C of undercooling. The crystals represent thin plates in the form of rhombs, triangles, or hexagons. The twinning on the transverse cross sections was observed at the study of microsections and cleaved facets. It turned out that the lamellar GaP crystals contain the plane of twinning, parallel to the planes (111).

The growth process of lamellar crystals can be formally divided into two components: the tangential growth in the plane (111) and layer-by-layer growth in the direction normal to the plane (111). Because the ratio of Ga and P atoms differed significantly from the stoichiometry, it is assumed that diffusion is the process that determines the rate of growth.

Since the formation of the initial crystals occurs in a very short time, the growth in the tangential direction is difficult to control. The growth in the direction normal to the plane (111) is sensitive to the fluctuations of the degree of supersaturation, resulting from the thermal motion of atoms and temperature fluctuations.

Thus, deteriorations of quality or shape of defects of GaP plates during their growth from Ga-P melt solution were observed in the following cases: (1) at a considerable increase of concentration of impurities in the GaP solution and dependently on the chemical nature of the chosen impurity and (2) at the change of the crystallization conditions, namely, at the sufficient deterioration of the cooling velocity control or in the case of nonuniform heat removal from the container for the crystal growth.

Processes for the formation of dendritic needles and their transformation to platelet crystals take place over a small temperature and time interval. As a result, they are hard to control, while crystal growth is easily controlled in the direction normal to the plate (111), due to the sensitive nature of velocity of the solution cooling and accuracy of the temperature control [1, 3].

The above-stated results imply that only high-quality and carefully controlled growth equipment will yield the highest-quality GaP crystals. However, despite these precautions, we show how to considerably increase the quality and utility of these freshly prepared GaP crystals.

B. Optical properties of perfect GaP:N crystals

Investigating gallium phosphide (GaP) crystals grown by one of the authors in the 1960s, clear improvement of their optical and mechanical properties was noted for the first time only after 10-12 years. It was unusual and interesting in the situation when all inorganic nature around us usually deteriorates in time. Therefore, the decision was taken to investigate, to understand, and to use this phenomenon in the future.

Figure 1 provides a comparison of the evolution in luminescence spectra at low temperatures (80 K and below) from GaP:N over a period of 25 years. It is seen over this period zero-phonon line A of single N-impurity-bound excitons and their phonon replica are narrower in their line widths when compared to the freshly prepared single crystals. Further, as expected, zero-phonon line and replica in samples aged at room temperature for 25 years shift spectral position depending upon the concentration of N impurities (Figure 1b, spectra 1-3) according to Refs [1-5], while the same freshly prepared crystals exhibited broader luminescence line widths with increasing nitrogen content (Figure 1b, spectrum 4). These, along with other half-centennial findings, including modifications in luminescence kinetics, spontaneous Raman scattering, X-ray diffraction, absorption spectra, micro-hardness, and density of dislocations, that are reported elsewhere [1-5], strongly suggest that close-to-ideal GaP:N crystals form over time due to the equally spaced disposition of N impurities instead of their chaotic distribution in the same freshly prepared crystals.

As noted in Ref. [2], these results suggest a new type of crystal lattice in which the host atoms occupy their proper (equilibrium) positions in the crystal, while the N impurities are periodically substituted into the lattice portion into short chains of equal length. According to the data obtained from Raman light scattering, host atoms of this new lattice develop harmonic vibrations, and high degree of lattice perfection leads to an abrupt decrease in the non-radiative recombination and an increase of efficiency and spectral range of luminescence.

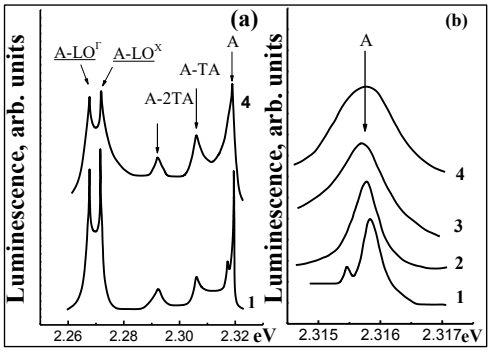

Fig.1. Evolution of the GaP:N luminescence with time and nitrogen concentration at the temperature of 15 K. (a) Zero-phonon line of the bound exciton A and its transversal acoustic (TA) and longitudinal optic (LO) phonon replica in as prepared (4) and 25-year long-term-ordered (1) crystals. (b) Zero-phonon line A as a function of nitrogen (N) concentration. 1-3: 25-year-old crystals. 4: as-prepared. Curves 1 through 4 represent samples with nitrogen concentrations of 10^{17}, 10^{18}, 10^{19}, and 10^{18} cm^{-3}, respectively [2, 5].

As was shown in Ref. [2, 5], the GaP:N crystals aged for at least 40 years possess no discrete impurity level for N-bound excitons in the forbidden gap. They also demonstrated a uniform luminescence from a broad excitonic band instead of the narrow zero-phonon line and its phonon replica as observed from the less-aged, 25-year-old crystals. Stimulated emission of light in these temporally ordered crystals (Figure 2b) also is observed.

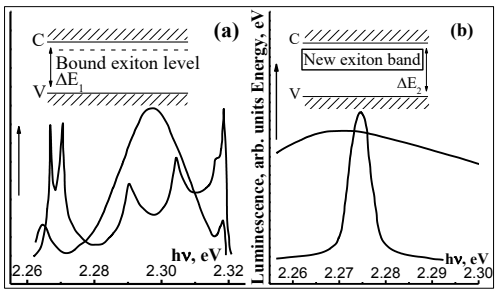

Fig.2. Luminescent spectra and schematic representation of the forbidden gaps (ΔE_1, ΔE_2) in the nitrogen-doped GaP aged for (a) 25 years and (b) 40 years [2, 5].

Thus, long-term-ordered GaP:N crystals demonstrate uniform bright luminescence from a broad excitonic band instead of the narrow zero-phonon line and its phonon replica in disordered and partly ordered (25-year-old) crystals. This is due to the fact that ordered crystals have no discrete impurity level in the forbidden gap. To the best of our knowledge, such transformation of a discrete level within the forbidden gap into an excitonic band (Figure 2a, b) is observed for the first time. In this case, the impurity atoms regularly occupy the host lattice sites and affect the band structure of the crystals, which are now a dilute solid solution of GaP-GaN with regular disposition of N atoms instead of freshly prepared GaP doped by occasionally located N atoms. Note that the increase of luminescence excitation in case of partly ordered GaP:N (Figure 2a, dotted line) leads to a broad luminescence band as a result of bound exciton interaction, while in the case of perfectly ordered crystals (Figure 2b), one can see an abrupt narrowing of the luminescence band due to stimulated emission in defect-free crystals. Earlier, in freshly prepared crystals, we observed a clear stimulated emission from a GaP:N resonator at 80 K [5], as well as the so-called superluminescence from GaP single crystals having natural faceting. Presently, our ordered crystals have a bright luminescence at room temperature that implies their perfection and very low light losses. We demonstrate also that the stimulated emission in long-term-ordered GaP is also developed even at room temperature.

C. Excitonic crystal and its importance in optoelectronics

Doping of GaP with N leads to isoelectronic substitution of the host P atoms by N in its crystal lattice and to the creation of the electron trap with a large capture cross section. Therefore, any non-equilibrium electrons in the vicinity of the traps will be captured by N atoms, attracting non-equilibrium holes by Coulomb interaction and creating the bound excitons – short-lived nanoparticles with the standard dimension of the order of 10 nm (it is the Bohr diameter of bound excitons in GaP:N). Note that none of the nanotechnology methods are used in the creation or selection of dimensions of these nanoparticles – only natural forces of electron-hole interaction and electron capture by the traps are necessary for the creation of these nanoparticles. As a result, we get something like neutral short-lived atom analog – a particle consisting of heavy negatively charged nucleus (N atom with captured electron) and a hole. The so-called "zero vibrations" do not destroy possible solid phase of bound excitons having these heavy nuclei that give an opportunity to reach their crystal state – short-lived excitonic crystal.

Taking into account the abovementioned results, a model for the crystal lattice and its behavior at a high level of optical excitation for well-ordered N-doped GaP (Figure 3) can be suggested.

At the relevant concentrations of N, the anion sublattice can be represented as a row of anions where N substitutes P atoms with the period equal to the Bohr diameter of the bound exciton in GaP (approximately 10 nm) (Figure 3a). At some level of excitation, all the N sites will be filled by excitons, thereby creating an excitonic crystal (Figure 3b), which is a new phenomenon in solid-state physics and a very interesting medium for application in optoelectronics and nonlinear optics [2, 3, 5].

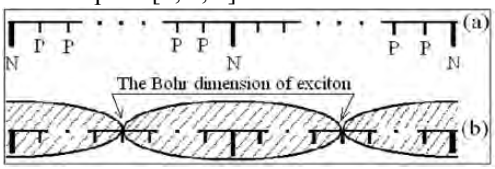

Fig.3. The models of the well-ordered GaP:N [34]. (a) The new type of crystal lattice with periodic substitution of N atoms for the host P atoms. (b) The excitonic crystal on the basis of this lattice. The substitution period is equal to the Bohr diameter of exciton (~100 Å), and optical excitation is enough for complete saturation of the N sublattice with nonequilibrium electron-hole pairs (see details in Refs [2, 3, 5]).

Thus, using bound excitons as short-lived analogs of atoms and sticking to some specific rules, including the necessity to build the excitonic superlattice with the identity period equal to the bound exciton Bohr dimension in the GaP:N single crystal, we get a unique opportunity to create a new solid-state media – consisting of short-lived nanoparticles excitonic crystal, obviously, with very useful and interesting properties for application in optoelectronics, nanoscience, and technology.

D. Current approach to selection of materials for electronics and new prospect

Properties that can be used to achieve light emission at a definite spectral region include:

(a) selection of the material on the basis of its band structure peculiarities and the value of the forbidden gap, which as a rule sizes up the maximum value of the emitting photons;

(b) doping of the selected material by impurities or, on the contrary, precise purification of the

chosen material for the creation of new channels of light emission; and

(c) selection of the temperature and/or excitation level that to change contribution of different channels into light emission due to their disappearance or saturation.

It is impossible or, at least, very difficult to realize all the the interestng optical properties in a single freshly prepared material. Therefore, the present technologies employ diverse range materials using very complicated and expensive technologies for their fabrication with the necessary application parameters. Down-selecting a set of various materials applied currently in optoelectronics at the maintenance or even improvement of their high parameters and quality is one of the most important goals for reduction in price and wide application in the practice of electronic

devices. The most impressive demonstration of this approach would be the selection of a single suitable material, the development of a peculiar technology of its preparation, its interesting properties and prospects for application in optoelectronics instead of a huge number of various materials and their technologies.

Sophisticated growth technique, knowledge of crystal growth mechanisms, of different processes, improving or deteriorating in time the prepared crystals, and the relevant comprehensive experience are necessary for the preparation of the perfect, free or almost free of contamination and doped GaP single crystals.

However, in the manufacture of artificial crystals, we are faced with the need to fabricate them for a very short time compared with the times for which naturally perfect crystals are grown. In such a short time, own atom or dopant diffusing through the crystal usually cannot absolutely exactly occupy the places intended for them in ideal crystal lattice. This gives rise to lattice defects, which, in turn, hinder the achievement of perfect devices. Manufactured on the basis of such materials, greatly reduce their lifetime, as well as make it impossible manifestation of some very interesting and useful for the application of the effects observed in advanced materials. Significant levels of funds are spent on searching and implementing methods for creating materials, not existing in the nature, that can, even if in a narrow field of application and at short time service, replace the material with a perfect crystal lattice and the necessary concentration and location of dopants. Hence, there is an urgent need to develop methods for the creation of an ideal semiconductor material the required parameters for use in electronics. In this case, it will disappear or substantially decrease the need to develop a plurality of individual costly technology to produce a plurality of different materials with a limited resource and service applications, and as a very important result for any country involved in the production and use of electronic materials – a giant savings and the possibility of redeployment to other needs of funds spent on the production of low-quality materials and products.

Using the long-term-ordered perfect GaP or similar on behavior and properties material in electronic industry instead of current elaboration of very expensive and labor-consuming technologies for diverse materials with their limited application spectral region and other parameters, we get a big commercial, scientific, and technology advantage from their fabrication and application.

The long-term, tens of years ordered GaP, its artificial analogs, and nanoparticles have very interesting properties, which give an opportunity to apply them in optoelectronics with high economic effect instead of a lot of different compounds currently used in optoelectronics.

III. CONCLUSIONS

Thus, our half-of-a-century collection of results provides a new approach to preparation of perfect optoelectronics materials and a unique opportunity to realize a new form of solid-state host – the excitonic crystal.

As noted in this article and the relevant references, high-quality material for industrial electronics can be prepared by storing freshly grown crystals in a special storage. Only perfect crystals with the attained necessary properties will then be periodically retrieved for device fabrication, while new portions of fresh crystals will be placed for ordering, as is done with wines and fine liquors.

All of the results presented here and included in summary reviews [1-5] may sufficiently change the approach to the selection of materials necessary for electronics, and to make cheaper and simpler technology for the preparation of the selected materials and device structures on which they are based. Our study of long-term convergence of bulk- and nanocrystal properties brings a novel perspective to improving the quality of semiconductor crystals. The author's unique collection of pure and doped crystals of semiconductors grown in the 1960s jointly with current efforts provides an opportunity to observe and to apply in optoelectronics the results of the the long-term improvement of properties in these key electronic materials.

ACKNOWLEDGMENTS

The authors are glad to note that the broad discussion and dissemination of their joint results stimulate further collaboration with reliable partners from the USA, Russia, Italy, Romania, France, and other countries.

We express the cordial gratitude to our teachers, world-known scientists late Profs Nina A. Goryunova, Nobel Prize Laureate Alexander M. Prokhorov, academicians Rem V. Khokhlov and Sergei I. Radautsan. We are very grateful to the US Department of State, Institute of International Exchange, Washington, DC, the US Air Force Office for Scientific Research, the US Office of Naval Research Global, Civilian R&D Foundation, Arlington, VA, to our colleagues and coauthors from Clemson University, SC, University of Central Florida, FL, Istituto di elettronica dello stato solido, CNR, Rome, Italy, Universita degli studi, Cagliari, Italy, Lomonosov Moscow State University, Joffe Physico-Technical Institute and State Polytechnic University, St. Petersburg, Ac. Scie. Institute of General Physics, Moscow, Russia, Institute of Applied Physics and Academy of Sciences of Moldova for support and attention to this protracted research.

REFERENCES

[1] S. Pyshkin, “Gallium Phosphide – New Prospect for Optoelectronics”, J. Advances in Optoelectronic Materials, vol. 1(4), pp. 59-66, 2013.

[2] S. Pyshkin, “Excitonic crystal and nanotechnology”, Nanosci Technol, vol. 1(2), pp. 1-5, 2014.

[3] S. L. Pyshkin, “Excitonic Crystal, Nanotechnology and New Prospect for Optoelectronics”, The Open Optics Journal, vol. 9, pp. 26-37, 2015.

[4] S. Pyshkin, “New Prospect for Optoelectronics”, Nanosci Technol, vol. 3(1), pp. 1-5, 2016.

[5] S. Pyshkin, J. Ballato, “Properties of GaP Studied over 50 Years”. Chapter 1, In: Optoelectronics – Advanced Device Structures, S.L. Pyshkin and J. Ballato (Eds), Rijeka, InTech, pp. 1-20, 2017.