Chapter 1

Introductory Chapter: Bound Excitons in Gallium Phosphide

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http://dx.doi.org/10.5772/intechopen.73550

1. Introduction

The authors contributing to InTech open access book *Excitons* offer exciting complementary perspectives on the progress in the field of excitons and their use in processes occurring in modern optoelectronic device structures. This is both an important and a complex field, as will be elaborated further on, which is why it has been chosen as an introductory stance to summarize some findings in the field made by the author of this chapter, also the editor of this particular book.

As we note the unprecedented interest of researchers from all over the world in using excitons in the development of modern optoelectronic device structures, we offer some of the results and material gathered in the process of our half-a-century long work for further study and application in electronic companies. The results presented here and in References to this Chapter are inspired by many outstanding scientists, my teachers and the colleagues, representing a number of scientific centers worldwide and in particular Russia, the USA, and Italy, who at various points made invaluable contributions to understanding and advancing the ideas on results obtained through the years of my research.

We have been growing and exploring gallium phosphide [1–8] for more than a half a century, a process of experimenting, analysis and observation which resulted in unique material reflecting previously unexplored properties of excitons and new prospects for the use of GaP, which could be very interesting for application in the electronic industry.

Studying and using new properties of excitons are a difficult task, mainly due to the low quality of freshly prepared semiconductor and other crystals. Fresh crystals are usually characterized with a large concentration of crystal structure defects, such as vacancies and dislocations

of the proper arrangement of intrinsic and impurity atoms in the GaP (face-centered cube) crystal structure. Notably, despite all efforts of crystal growth experts, it is virtually impossible to compete with natural crystals grown for thousands of years in favorable natural conditions. Large concentration of defects, noted above, inevitably arises from the rapid freezing of the constituent crystals of the atoms and the dopants in positions, which they occupy being in the liquid GaP phase at the time of the beginning of cooling and the formation of embryos, according to the adopted technology for obtaining crystals of GaP [1].

Natural tendency of own and impurity atoms to occupy the places assigned to them by the crystal lattice is hampered by their infinitesimally slow diffusion rate at room or at low temperature of storage of grown crystals. In this way, decades pass before the lattice component occupies the exactly correct position in the crystal lattice, diffusing inside it at the storage temperature, from the place where it was at the time of the onset of cooling of a mixture of GaP, necessary for the onset of deposition and further growth of pure or doped crystals (see details in [1–8]). Naturally, most crystal manufacturers are reluctant to wait for improvements in the structure and properties of imperfect crystals, as this process is extremely slow. This fact leads to the need of using noncompliant materials with poor parameters, which however drastically reduces the lifetime and quality of device structures made from them, and in addition increases production costs and sharply reduces the value of the output into the electronic industry. For instance, presently manufactured low-quality materials cause high margin of error in microchips resulting in quality problems with microelectronic-based devices, such as mobile phones and computers, but also devices used in "heavy" industries, such as healthcare, space, or defense. Due to the described limitations, the possibility of using excitons as the most vulnerable material easily destroyed by defects of photon carriers is significantly reduced.

Taking the aforementioned into account, we consider some properties of bound excitons in GaP, including the possibility and the expected results of their application in optoelectronic device structures. Recall that the term *bound exciton* means an electron-hole pair localized near the impurity center. In our case this is an isoelectronic impurity N replacing the own P atom in the GaP lattice, possessing a giant-capture cross section with respect to the free electron. The captured electron attracts a hole, forming a bound exciton.

The presence of a heavy nucleus (atom N^+ trapped electron) is an important feature of bound excitons, which, under appropriate conditions, allows them to form a solid exciton phase, in contrast to free excitons, where the transition to the solid phase is impossible due to the approximate equality of the effective masses of the electron and holes and so-called zero-point oscillations, which destroy our attempts to form a solid phase with further condensation of a system of coupled excitons. We also note the possibility of creating exciton crystals that arise in the ordered arrangement of impurity centers and the creation of an appropriate impurity sublattice with a crystal structure analogous to the GaP single crystal, but with a lattice parameter equal to the Bohr diameter of the bound exciton in this material (approximately 10 nm).

Keeping in mind possibly groundbreaking features (at least for some industries, we have already mentioned) of the solid exciton phase, we have focused our long-term technological efforts on obtaining perfect GaP crystals, including creation and investigation of the properties of perfect GaP crystals and certain device structures based on them. We have established that the mentioned above impurity sublattice arises with prolonged storage of GaP single

crystal plates under natural conditions (room temperature and normal pressure). According to our estimates [2, 6], the crystals must be 10–15 years old under these particular conditions. During this time, randomly distributed impurities form the correct crystalline sublattice at room temperature, due to the natural diffusion of impurities into places with their low concentration and their displacement to places that reduce mechanical tensions in the crystal. Despite the fact that this process takes over a decade, the qualities of the output material offer numerous opportunities in some of the key industries based on microelectronic technologies, especially strategic, long-cycle ones. Even though current expectations of the cycle of perfect crystal growth may last up to 15 years or more, we strongly believe that this long-term process can be significantly shortened by skillful selection of storage conditions (accelerating the diffusion temperature, applying counterpressure using the vapor of volatile components P, etc.). Masterful selection of storage conditions and the eventual drastic reduction in the time needed for obtaining close to ideal crystals, along with other factors considered below, incentivize to test and potentially introduce the proposed method of nearly perfect crystal growth into some key electronic industries and make devices of highest quality based on the top quality crystals.

In addition to the above, after 10–15 years from the beginning of the introduction of the proposed system for obtaining perfect crystals, there will be no need to wait for decades to "mature" them. This is possible provided that new materials are stored permanently and only materials that have been ripening for a certain period of time, which according to our estimates are 10–15 years old, are taken out for use.

In order to incentivize further interest, part of the methodology is described in short as follows. We have used a sublattice of N atoms at distance of 10 nm prepared in advance in the crystal and engaged powerful optical pumping with photon energy exceeding the width of the forbidden band of GaP and the power of light sufficient to fill all the impurity centers. In this way, we were able, for the first time in global practice, to obtain an excitonic crystal, schematically depicted in **Figure 1**. In addition, **Figure 1a** shows phosphorus host atoms P in the GaP crystal lattice and atoms of nitrogen impurity N periodically replacing them through 10 nm. The electrons trapped by the impurity centers and the holes interacting with them at corresponding excitation level form an excitonic crystal shown in **Figure 1b**.

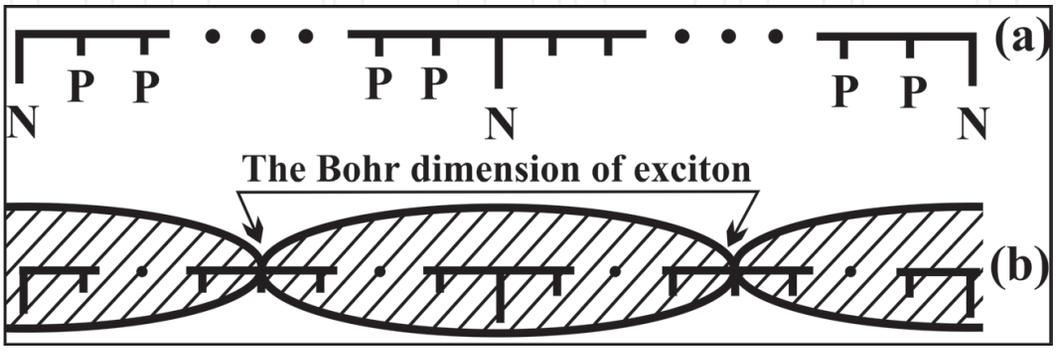

Figure 1. Models of the well-ordered GaP:N [4, 8]. (a) The new type of crystal lattice with periodic substitution of N atoms for the host P atoms. (b) The excitonic crystal on the basis of this superlattice. Substitution period is equal to the Bohr diameter of exciton (~100 Å), and optical excitation is enough for complete saturation of the N sublattice with nonequilibrium electron-hole pairs (see details in Ref. [8]).

Note that none of the nanotechnology methods are used in the creation or selection of dimensions of these nanoparticles but only natural forces of electron-hole interaction. As the result, we get something like a neutral short-lived crystal nuclei (N atoms with captured electrons) and holes, interacting with them through Coulomb forces. The so-called zero vibrations do not destroy this solid phase of bound excitons having these heavy nuclei that give an opportunity to reach their crystal state—short-lived excitonic crystal.

It is interesting to compare the luminescence of freshly prepared, partially (a) and ideally ordered GaP:N (b) crystals presented in **Figure 2**.

We note that the same freshly prepared crystals do not possess any luminescence at all because of the enormous number of defects that supply the radiationless return to the valence band of electrons excited by light. The same partially ordered crystals exhibit a luminescence spectrum of excitons consisting of a zero-phonon line and its phonon satellites in the emission of the intrinsic acoustic and optical phonons of the GaP lattice (**Figure 2a**).

Earlier, we observed a clear stimulated emission from a GaP:N resonator at 80 K [4] in freshly prepared crystals, as well as the so-called superluminescence from the GaP single crystals. Presently, our ordered crystals have a bright superluminescence at room temperature that implies their perfection and very **lower** light losses. Thus, we demonstrate that stimulated emission is developed even at room temperature by direct electron-hole recombination of an electron at the bottom of the conduction band with a hole at the top of the valence band and the LO phonon absorption.

We also note an interesting analogy between the radiation of a well-ordered and perfect GaP crystal and well-prepared nanoparticles based on it, which we present in **Figure 3**.

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

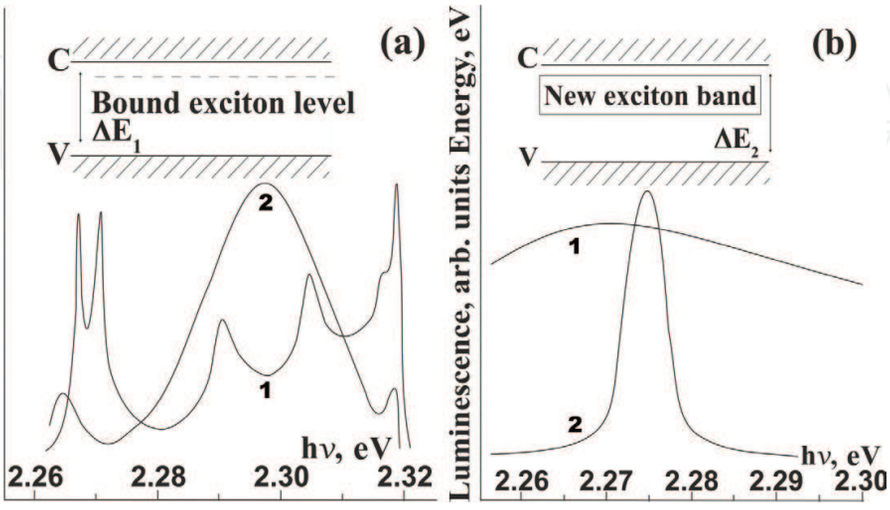

Figure 2. Luminescent spectra and schematic representation of the forbidden gaps (ΔE1, ΔE2) in the nitrogen-doped GaP aged for (a) 25 years and (b) 40 years.

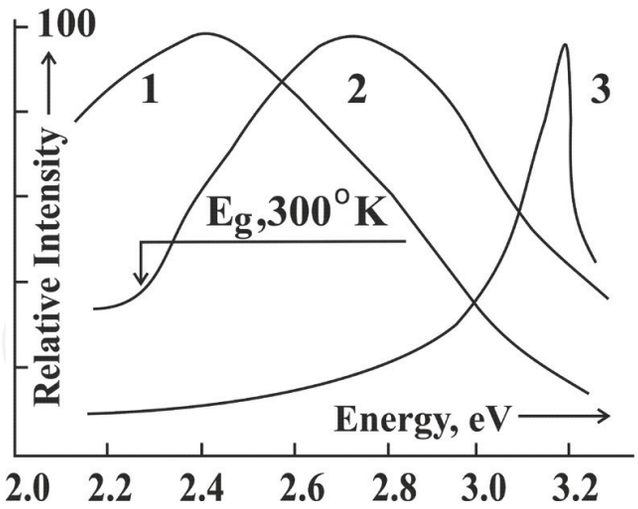

Figure 3. Luminescence of perfect bulk GaP single crystals [1] in comparison with the luminescence of GaP nanoparticles and GaP/polymer nanocomposites [2, 3]. Prepared by us, nanoparticles [5, 7] were stored as dry powder (spectrum 2) or suspension in a liquid (spectrum 3).

Acknowledgements

We are happy to note that the broad discussion and dissemination of our joint results stimulate further collaboration with our partners from the USA, Russia, Italy, Romania, France, and other countries.

Prof. Sergei L. Pyshkin expresses his cordial gratitude to his teachers, renowned scientists late Prof. Nina A. Goryunova, Nobel Prize Laureate Alexander M. Prokhorov, and academicians Leonid V. Keldysh, Rem V. Khokhlov, and Sergei I. Radautsan, as well as 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; the US Science & Technology Center in Ukraine; his 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 Polytechnical University, St. Petersburg; Ac. Scie. Institute of General Physics, Moscow, Russia; and Institute of Applied Physics and Academy of Sciences of Moldova for support and attention to this protracted (1961 to present time) research.

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