OPTICAL AND MECHANICAL PROPERTIES OF LONG-TERM ORDERED SEMICONDUCTORS

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Abstract

The 45-year-monitoring of optical and mechanical properties of the various semiconductor crystals grown in the sixties of the past century shows that the stimuli for long-term improvement of crystal quality prevail over those which lead to its degradation.

Evolution of optical and mechanical properties testifies that now in diamond-like gallium phosphide (GaP) doped with nitrogen (N), the impurity is a regular element of the new crystal lattice - it increases the forbidden gap, and at relevant concentration and level of optical excitation creates a bound excitonic crystal. The ternary compound $CdIn_2S_4$, now having the perfect normal (instead of partly inversed) spinel crystal lattice, as well as GaP with evenly distributed impurities, demonstrate new stable and bright luminescent phenomena, including stimulated emission and "hot" luminescence at room temperature. All chosen semiconductor crystals from different groups of semiconductor compounds demonstrate the long-term ordering and improvement of useful for application properties.

Existing technologies help us to reproduce artificially these naturally ordered structures for application in optoelectronics.

1. Introduction

Single crystals of semiconductors due to relatively fast processes of their growth contain a lot of different defects such as wrong positions of host and impurity atoms, vacancies, dislocations, impurity clusters, etc. All that are the reasons for deterioration of crystal lattice, the change for the worse of mechanical, electric and optical properties of materials, and quick degradation of devices made on their base.

However, there are the long-term natural stimuli for right and ordered distribution of impurities and host atoms in a crystal, such as their diffusion along gradient of concentration, trends to relaxation of the mechanical strength around clusters as well as the minimum of free energy at correctly oriented chemical bonds between host atoms.

In our presentations [1], we have compared for the first time the app. 25-year-long processes of the impurity ordering in GaP and evolution of the antistructural defects of the type of Cd_{In} and In_{Cd} in $CdIn_2S_4$. Continuing in 2001–2008 the monitoring of the single crystals [2-4] grown app. 40 years ago [5], we studied their changing with time luminescence, Raman light scattering and microhardness in comparison with the data obtained from the same crystals

since the sixties of the past century [6] as well as with the properties of nanocrystals [7] and freshly prepared bulk single crystals [4]. We show that the long-term natural stimuli improving perfection of our crystals prevail over others which could lead to heterogenic systems. It means that new ways for fabrication of semiconductor devices with high and stable in time characteristics really do exist. The results of luminescence, Raman light scattering, and microhardness, in addition to those described in previous papers [1-4, 6, 7], were presented at the 4th International Conference on Materials Science and Condensed Matter Physics (Chisinau, Republic of Moldova, 2008) and in this work.

2. Experimental results and discussion

2.1. GaP

Measurements of luminescence show that app. 25 years after the preparation of the crystals (1963-1966) the zero-phonon line A of single N impurity-bound excitons and its phonon replica become narrow and the background of the spectrum is low (Figs. 1a, 1b, spectrum *1*), while the freshly prepared crystals develop broad emission lines and a remarkable background (Figs. 1a, 1b, spectrum *4*). Zero phonon line A and its phonon replica in the aged crystals shift their positions with the concentration of N impurities (Fig. 1a, spectra *1-3*) according to the known dependence. Compared with ordered GaP:N, fresh crystals demonstrate only broadening of the lines when the nitrogen concentration increases (Fig. 1a, spectrum *4*). This confirms ordered disposition of N impurities with equal spacing between the impurity atoms in the aged crystals.

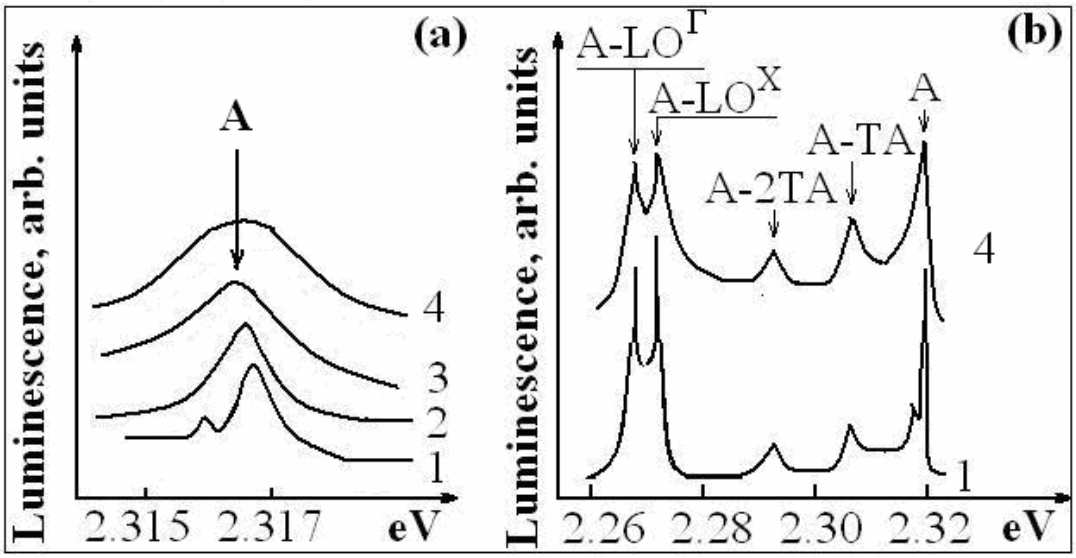

Fig. 1. Zero-phonon line of bound excitons A as a function of N concentration: (a) 15 K. *1-3*: 25 years ordered crystals. *4*: unordered. *1-4*: No = 10^{17}; 10^{18}; 10^{19} and 10^{18} cm^{-3} concentration of N, respectively. (b) 15 K. Zero-phonon line A and its TA and LO phonon replica for 25 years ordered (*1*) and freshly prepared (*2*) crystals.

Figure 2a demonstrates differences in luminescent spectra of fresh (spectrum *1*), app. 25 (*2*) and 40 years (*3*) ordered GaP crystals doped with nitrogen (GaP:N). There are no qualitative differences in the luminescent spectra *1* and *2* obtained from freshly prepared and 25 years old ordered crystals. Only the narrowing of the lines and their clearly observed shift with N concentration testify to improvement of the host lattice and equal spacings between impurities.

However, the luminescent spectrum of the same GaP:N crystals after 40 years ordering at normal temperature and pressure conditions (spectrum *3*, Fig. 2a) is absolutely different from those measured right after the growth of single crystals or during 25 years of their ordering. Now instead of narrow lines of bound excitons, one can see only a continuous bright broad band. Increasing the level of excitation, we easily obtain an abrupt narrowing of the band as a result of stimulated light emission.

Thus, the 40 years ordered GaP:N crystals have no discrete impurity level in the forbidden gap and demonstrate the uniform luminescence or stimulated emission from a broad excitonic band instead of narrow zero-phonon line and its phonon replica in unordered and partly ordered (25 years old) crystals.

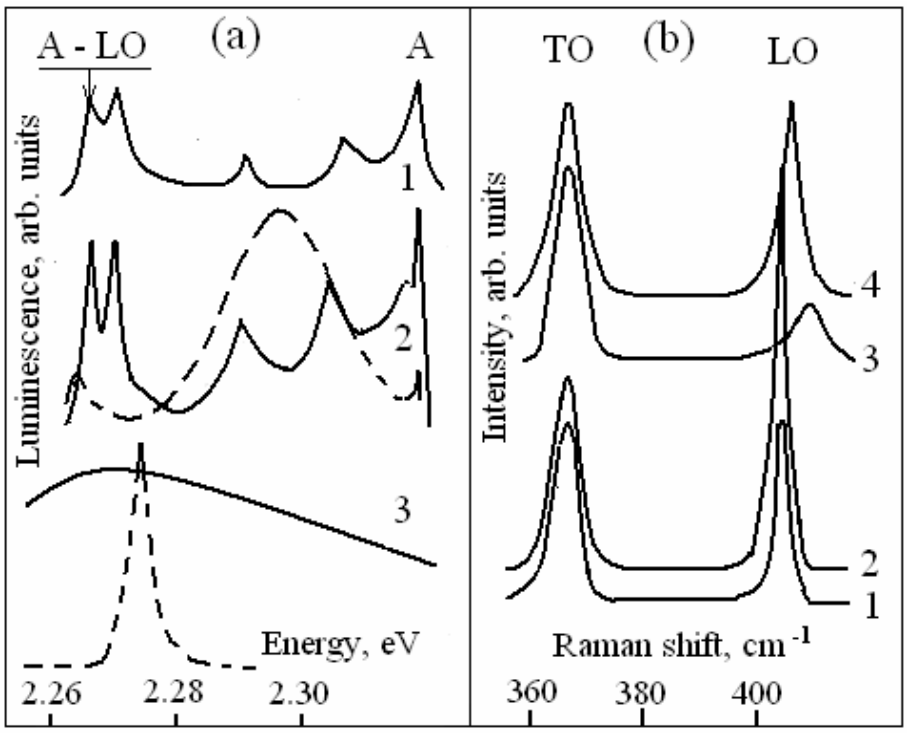

Fig. 2. Evolution of the GaP luminescent (a) and Raman light scattering (b) spectra with time and N concentration: (a) GaP doped with 10^{18} cm-3 of nitrogen. Zero-phonon line of the bound exciton A and its transversal acoustic (TA) and longitudinal optic (LO) phonon replica of unordered freshly prepared (*1*), app. 25 (*2*) and 40 (*3*) years old ordered crystals. 15-30 K. GaP nanoparticles have the same spectrum *3* as the 40 years old ordered bulk crystals. The dotted lines correspond to highly optically excited crystals. (b) Raman light scattering spectra in GaP of 40 (*1, 2*) and 25 (*3, 4*) years old ordered crystals. *1* and *4* stand for pure GaP; *2* and *3*, for GaP heavy doped with N. 15 K.

Uniform substitution by N impurities of P host sites leads to a new type of crystal lattice. This new crystal lattice with the impurities as its intrinsic component has an outstanding perfection confirmed also by our experiments in Raman light scattering. Difference in the present perfect state of the crystal lattice in comparison with the data obtained with the same crystals and conditions in 1989–1993 [1, 6] can be seen from Fig. 2b, which shows the relevant Raman spectra of pure GaP and GaP:N [2-4].

Figure 3a shows that in the freshly prepared and partly ordered GaP:N crystals, the position of the absorption edge does not depend on N impurity concentration; at the same time, under the conductance band, this impurity creates the 21-meV energy level for bound exciton both for freshly prepared and for 25 years ordered crystals. On the contrary, the GaP:N crys-

tals ordered for app. 40 years demonstrate an increase of the forbidden gap value (curve *1* in Fig. 3a), which is proportional to the N concentration according to the Vegard's law, like to a dilute GaP-GaN solid solution. Therefore, nitrogen looses impurity status and, as an element of the new crystal lattice, creates an additional broad band under the bottom of the conductance band where the N bound excitons are localized before annihilation.

Investigating the dependences of the absorption edge position on N impurity concentration (Fig. 3a), microhardness, and density of dislocations (Fig. 3b), we have found a tight connection between long-term evolution of optical and mechanical properties of GaP as well as a considerable difference in characteristics of freshly prepared and long-term ordered pure and doped crystals [2-4].

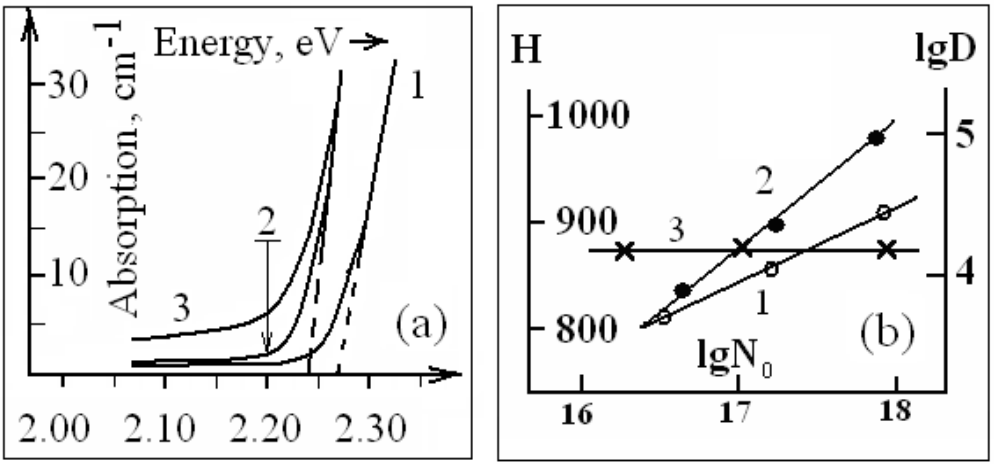

Fig. 3. 40-year-evolution of the absorption edge (a), microhardnes H, and density of dislocations D (b) in GaP undoped or doped with different nitrogen concentration N_0: (a) Absorption coefficient in long-term ordered (40 years) GaP:N (*1*) and in 25 years old (*2*) or freshly prepared undoped GaP (*3*). N concentration in *1* is about 10^{18} cm-3; (b) *1* denotes microhardness H in freshly prepared unordered crystals as a function of N concentration; *2*, the same for 40 years ordered crystals; *3*, D as a function of N concentration.

According to the classic point of view [8], a good plasticity is determined by free movement of dislocation through the crystal body under its mechanical loading. Impurities brake the movement of dislocations. Therefore, the value of microhardness H clearly depends on impurity concentration (Fig. 3b, lines *1* and *2*); relatively pure crystals have the minimum of microhardness. Increase of the impurity concentration in GaP crystals doped with N, Bi, N:Sm and a lot of other chemical elements, substituting the host atoms (N, Bi) or occupying the interstitials in the crystal lattice (Sm), leads to the relevant increase of microhardness (see Figure 3b, lines *1* and *2*, respectively). We suppose that rather high difference in microhardness of the long-term ordered highly doped and freshly grown crystals can be explained by the effects of dense regular disposition of impurities and the crystal lattice modified by impurities in ordered crystals that creates a more serious obstacle to the dislocation movement than the system of the same impurities and of the same concentration disposed in the form of clusters with the intervals sufficient for gliding of dislocations.

Finally, line *3* in Fig. 3 shows that the density of dislocations D does not depend on time (during app. 50 years), concentration of the impurities, or the character of their distribution along the crystal. Only the chosen method of crystal growth determines the density of dislocations, while the very high quality of our equipment for growth of GaP crystals and special measures for precise regulation of the temperature during the growth considerably decrease the density of dislocations.

Thus, taking into account the above mentioned results, for the long-term (app. 40 years) perfectly ordered GaP doped with ~10^{18} cm^{-3} of N, we can suppose the models of crystal lattice and its behavior at high level of optical excitation (Fig. 4). At this concentration of N, the anion sublattice can be presented as a row of anions where N substitutes for P atoms with the period equal to the Bohr dimension of bound exciton (app. 100 Å) (Fig. 4a). At some level of excitation, all the N sites will be filled by excitons creating an excitonic crystal (Fig. 4b) - an absolutely new phenomenon in solid state physics and a very interesting medium for application in optoelectronics and non-linear optics.

Due to the high concentration of defects and highly intensive non-radiative recombination of the non-equilibrium current carriers, initially and for a long time, the luminescence of fresh doped and undoped crystals has been observed only at the photon energies less than the value of the forbidden gap and at temperatures of 80 K and below.

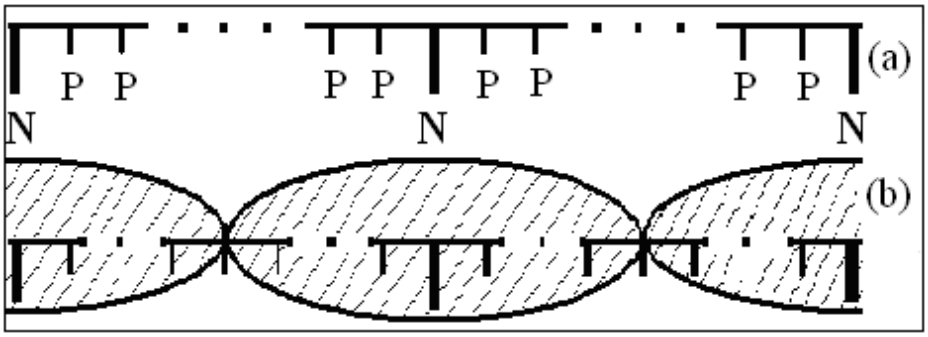

Fig. 4. The models of 40 years ordered GaP doped with N: (a) The new type of crystal lattice where the host P atoms are periodically substituted by N atoms; (b) Exciton crystal on the base of this crystal lattice. The substitution period is equal to the Bohr dimension of exciton, and optical excitation is sufficient for complete infill of the N sublattice.

Now luminescence of the long-term ordered bulk perfect crystals similar to the GaP nanocrystals is clearly detected in the region from 2.0 to 3.0 eV at the room temperature [2, 3]. We suppose that, in perfect bulk crystals, this considerable extension of the region of luminescence at 300 K to the high energy side of the spectrum is due to a very low concentration of defects and the relevant low contribution of non-irradiative electron-hole recombination, considerable improvement of crystal lattice, high transparency of perfect crystals and the lattice phonon absorption in indirect transitions at 300 K.

35 years ago, for the first time, we reported on stimulated emission in GaP [9]. Then the laser action was only observed in a highly optically excited good resonator of GaP at radiative recombination of bound excitons with the LO phonon emission and the temperatures of 80 K and less. But now we have a perfect single crystal and its bright luminescence is observed at room temperature and in a broad energy band.

Presently the stimulated emission is developed at direct electron-hole recombination and absorption of LO phonon. It is due to the following (1) the phonon participation is necessary for conservation of the moment in indirect optical transitions between band extrema in GaP, and (2) at room temperature the absorption of phonons from the heated crystal lattice is more preferable than their emission at electron-hole recombination.

Luminescent spectra of GaP crystals doped with N and Sm are very interesting. Similar to GaP and GaP:N, for the first time, GaP:N:Sm crystals were investigated when their luminescence could be observed only at 80 K and below [10]. As in 1975, the luminescent spectrum also consists of two parts, but, instead of narrow N bound excitonic lines and Sm peaks, we see a broad green excitonic band and the broad red-and-yellow band without any fine structure.

Note that the efficiency of Sm excitation at the N bound exciton recombination highly depends on degree of uniformity of the N-Sm mixture. The long-term ordering (during the period of 1963-2008) of the lattice gives a uniform mixture of Sm and N impurities in a perfect GaP crystal and, according to R.L. Bell [11], it provides up to 100% quantum efficiency of radiation from GaP:N:Sm system and bright luminescence at 300 K. The ratio of intensities of the green and red-and-yellow maxima depends on concentrations of N and Sm impurities as well as on level of excitation. At a chosen level of excitation and N/Sm ratio of concentration, one can obtain pure red or green emission of high efficiency or any combination of these colors, which is an important property of a tunable light source.

2.2. $CdIn_2S_4$

Redistribution of Cd and In along cation sublattice for a long time period has been investigated. As we have shown earlier [12], optical properties and quality of crystal lattice of $CdIn_2S_4$ highly depend on position and concentration of intrinsic structural and antistructural defects. Stoichiometric disturbances in the inherent structural defect concentration result in the appearance of two deep luminescent centres, one of them with the maximum at 1.45 eV and the other one at 1.65 eV, respectively, due to In vacancy in tetrahedral and octahedral anion sites of this spinel structure. Due to wrong positions of cations, $CdIn_2S_4$ has partly inverse spinel structure instead of normal spinel and antistructural defect (In_{Cd}, Cd_{In}) concentration depending on the growth condition up to $10^{20}cm^{-3}$ [13].

Figure 5a shows that the freshly prepared and then slowly cooled, as well as the long-term ordered crystals having a small concentration of the antistructural defects, contrary to quickly cooled crystals, develop fine structure of the luminescence due to interaction of electrons only with lattice phonons.

Analysis both of luminescence and Raman light scattering spectra [14, 15] shows that, due to the long-term ordering, the partly inverse spinel T_d^2 turns into the normal spinel structure O_h^7.

Exactly as in GaP, a phonon mode is broad and weak for freshly prepared $CdIn_2S_4$, but after the long-term ordering this peak is more intense, has a symmetric shape and small linewidth, characterizing harmonic vibrations in a perfect lattice (Fig. 5b, curves *1* and *2*, respectively). The crystals also develop stimulated emission and bright luminescence at 300 K (Fig. 6). Microhardness of the long-term ordered crystals has interesting features, which will be described in a separate paper. All that is a consequence of the ordered position of the defects inherent to $CdIn_2S_4$.

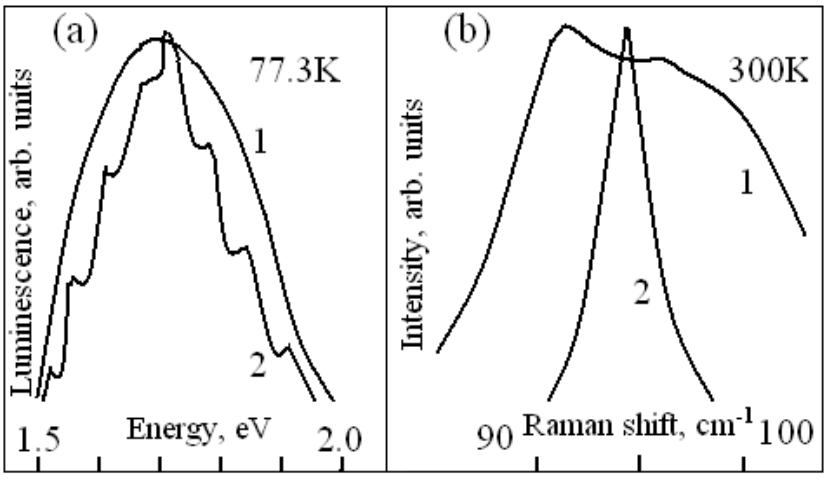

Fig. 5. Luminescence and Raman light scattering in $CdIn_2S_4$: (a) Luminescent spectra of the freshly prepared and long-term ordered $CdIn_2S_4$ crystals. Rapid (*1*) and slow (*2*), less than 5°C per hour, cooling rates. Ordered crystals develop a spectrum like *2*. (b) Raman light scattering at 92 cm^{-1} of unordered (*1*) and ordered (*2*) crystals. Excitation wavelength: 488 nm (a) and 514 nm (b).

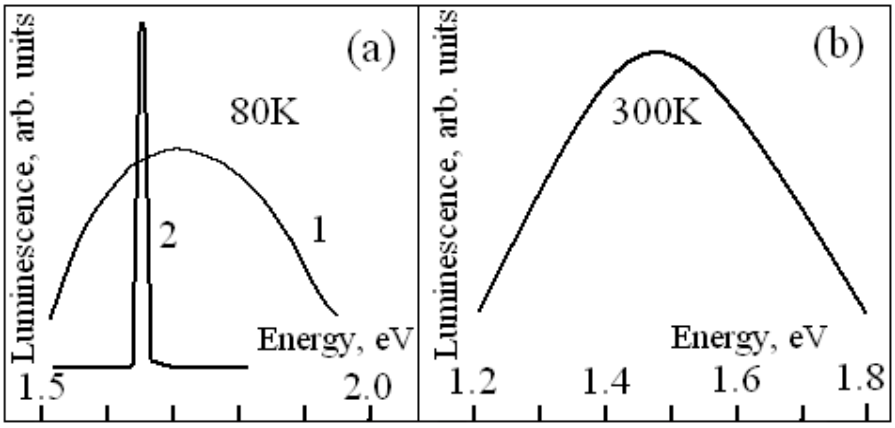

Fig. 6. $CdIn_2S_4$. Stimulated light emission (a) and luminescence (b) of the long-term ordered crystals. *1* and *2* differ in excitation intensity. Excitation wavelength: 530 nm.

3. Artificial multi-layered analogues of long-term ordered single crystals

With the significant recent progress in thin film deposition and growth techniques, there is obviously no longer a need to wait for such long-term ordering of a crystal lattice and impurities in order to prepare new device structures for optoelectronics. The problems which may be solved by the method of film deposition described below are the perfect conjugation of materials with different type and identity parameter of crystal lattice in heterostructures for emission or receiving of light, with its processing in a necessary digital form, growth of artificially ordered GaP:N system to generate a crystal-like excitonic phase, or preparation of nanolayers with the quantum confinement effect expanded and increased in comparison with the classic one.

This method elaborated by us is the laser assisted epitaxy (LAE) in combination with molecular beam (MBE) or metal organic vacuum phase (MOVPE) epitaxies (see, e.g., [12]). This method is highly efficient for growth and *in situ* characterization of advanced single and double heterostructures from materials having a great (more than 1%) mismatch of lattice period, for instance, Si/GaAs, Si/InP, Si/(Ca, Sr, Ba)F_2/ InP, and other advanced III-V and dielectric crystalline films onto Si or III-V substrates for 3-D optoelectronic integral circuits (OEIC). From the material gained from the target we can obtain by laser evaporation the beam of particles of laser-produced plasma having very high kinetic energies. It gives an opportunity to re-evaporate a part of the substance from the substrate surface, intermix it with the particles of the target before the substrate, and then to deposit again this mixture onto the substrate. The layer, growing pulse by pulse of laser irradiation, consists of a continuous row of solid solutions from pure target material on the surface of the growing film up to pure substrate material in the depth of the substrate. This intermediate thin (10-100 nm) layer (primer), which is located between the materials of substrate and evaporated target, smoothly conjugates lattice periods, mechanical and thermal properties of the heterostructure components. The intermediate layer (primer) is the base for further growth of the upper layer with perfect parameters for application.

Note that the perfect InP, GaAs, and other III-V films onto Si substrates were prepared by us [16, 17] many years before recent achievements in this direction at Motorola [18]. The same problem of the lattice mismatch in a semiconductor-dielectric-semiconductor (SCDS) structure, for instance, Si/SrF2/InP(100), was solved by MBE growth onto Si of (CaF_2-SrF_2) solid solution with the subsequent growth of InP film by combined MBE and LAE method [19].

The described method, due to its ability for fine regulation of the thickness of the pulse by pulse growing layer, can be efficiently applied to fabrication of the superlattice from GaP doped with N with the period of the order of the Bohr dimension of bound exciton (10 nm). This makes it possible to obtain a new optic medium—the one-dimensional excitonic crystal having a very low threshold for non-linear optic phenomena.

Further, preparation of a two-dimensional arrangement of N impurities in a GaP film is difficult but also possible with the help of ion lithography. Certainly, nowadays this technique is the frontier of technological possibilities, but, within the next few years, some very important results are likely to be obtained in this field. Using LAE, one can construct a new type of nanostructures on the base of two or a few different materials which will form a continuous row of solid solutions along the nanolayers or a substance with the composition necessary for application.

4. Conclusions

The unique collection of pure and doped semiconductor crystals grown in the sixties of the past century provides us with an opportunity to observe long-temporal evolution of properties of these key electronic materials. In the upshot of almost semi-centennial systematic investigation, we have established the main trends of this evolution. It was shown that the stimuli to improvement of quality of the crystal lattice are the consequence of natural thermodynamic reasons and prevail over the trends to destruction and deterioration of the crystals.

For the first time, we can observe a new type of the crystal lattice in which the host atoms occupy their right (equilibrium) positions in the crystal field, while the impurities periodically incorporated into the lattice divide it in the short chains of equal length, where the host atoms, according to the data obtained from Raman light scattering, develop harmonic vibrations. This periodical substitution of host atoms by an impurity turns the impurity into an element participating in the formation of energy bands of the crystal and leads to the change of the forbidden gap value and to the appearance of a broad energy band instead of the energy levels of bound excitons inside the forbidden gap, as well as to the change of the standard shape of their luminescent spectra (the bands instead of narrow lines).

High perfection and unique properties of this new lattice lead to the abrupt decrease in the contribution of non-radiative mechanisms to recombination of non equilibrium electron-hole pairs, to the relevant increase in efficiency and spectral range of luminescence equally at low and room temperature, and to the stimulated emission of light due to its amplification in the well arranged defect-free medium of the crystal. In the case of simultaneous doping of GaP with N and Sm, long-term ordered crystals develop a high efficiency of interaction of N exciton traps with Sm co-activators which gives bright luminescence at the room temperature and provides a simple way by means of the excitation intensity to switch the luminescent maximum between yellow and red and between green and blue regions.

Elaboration of technologies for growth of film and bulk crystals with ordered distribution of impurities and right localization of host atoms inside the lattice is our top-priority problem.

Results of regular long-term observations of very exciting changes happening with our unique collection of GaP single crystals give useful recommendations and a new approach to the future generation of opto- and microelectronic devices. They are used in development of the above noted new combined growth technique compatible with built-in ion lithography for fabrication of advanced light-emitting and photosensitive devices.

The combined method of the laser assisted and molecular beam epitaxies elaborated by us will be applied for fabrication of device structures with artificially ordered impurities; equally with classic methods, they will be used for preparation of new types of nanostructures.

Our work has been being carried out for years; however, the results most important for device application will be obtained only with recent progress in preparation of film and multi-layered structures. We hope they will have significant commercial value, because they provide an absolutely new optical medium and genuine product.

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