

Preparation and Characterization of Nanocrystalline GaP

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ABSTRACT

Nanoparticles of GaP have been prepared by the methods of mild aqueous synthesis, gas transport reactions and laser assisted deposition. Transfer of Ga and P by iodine and the next synthesis create onto a substrate a system of nanoparticles with the design and dimensions controlled by temperature. Interaction of laser plasma produced of a GaP target with a Si substrate creates the layer of nanoparticles with dimensions controlled by temperature, while the composition of them is (GaP) – (Si) solid solutions consisting of pure Si at the border with the substrate up to pure GaP at the surface of the layer. Spectra of luminescence and Raman light scattering of the particles prepared by these methods have been compared with those from perfect bulk crystals. Obviously, this new subject – the ordered mixture of nanoparticles with variable chemical composition gives additional opportunities for the shift and broadening of fluorescent spectra compared with the initial bulk materials.

Keywords: GaP, aqueous, gas transport, laser assisted synthesis

1 INTRODUCTION

This team has demonstrated previously [1, 2] that composites comprised of luminescent GaP nanoparticles could be of significant interest to the optical and optoelectronic industry. Even though bulk and thin film GaP has been successfully commercialized for many years the concept of nanocomposites as a new optical medium for accumulation, conversion and transport of light energy are only now receiving attention.

Due to quantum confinement effects [4] the optical properties of GaP nanoparticles with dimensions on the order of the Bohr exciton (app. 10nm) or less will be considerably different from those of bulk crystals. For this reason, this work seeks to expand further the applications of GaP itself through the formation of nanocomposites. Efforts undertaken were the preparation of nano particles with the controlled dimensions by a classic method such as the aqueous synthesis [5] and their characterization by TEM, XRD, Raman scattering and luminescent methods.

However, the main goal here is to present the results of long-term ordering in GaP single-crystals [6, 7] and some elaborated by us in the past [8] modifications of the methods of gas transport reactions and laser assisted growth of nano layers [9-11] that to propose them as the next steps in the development and application of this important area for research.

2 EXPERIMENTAL. DISCUSSION

The methods of preparation of GaP nanoparticles are described in a number of papers [5, 12-16]. Here we note only some essential details of used by us the aqueous synthesis as the base for comparison with the discussed below proposed methods.

NaOH pellets were dissolved in distilled water. Ga₂O₃, red phosphorus powder and I₂ were mixed and added to the NaOH solution. The mixed solution was then placed into an autoclave and heated there in an oven for 8 hours at 200 °C. After the completion of heating the autoclave was taken out of the oven and cooled. The obtained powder was filtered, washed with ethanol and dried. The dried powder was then annealed for 30 min in a furnace at 800 °C and then characterized using standard methods of XRD, TEM, Raman scattering and photoluminescence. The instruments for Raman light scattering and luminescence included spectrographs interfaced to a liquid nitrogen-cooled detector and an argon ion laser or lamp excitation sources. The spectra of Raman scattering was obtained at room temperature by excitation with 514.5 nm radiations and calibrated with the relevant etalons. Luminescence was excited by UV light of the lamps and measured at room and liquid nitrogen temperature.

2.1 Characterization of GaP Nanoparticles Obtained by Aqueous Synthesis

Figure 1 shows the TEM image of GaP nanoparticles obtained by the aqueous synthesis. One can see clusters with the dimensions of the order of 100 nm composed of GaP nanoparticles, having characteristic dimensions less than 10 nm. **Figure 2** demonstrates a considerable shift of the luminescence of nanoparticles to high energies of photons compared with the luminescence of pure bulk GaP

crystals - the nano crystals have the maximum of luminescence at 2.35 eV instead of 2.1-2.2 eV characterizing the bulk material.

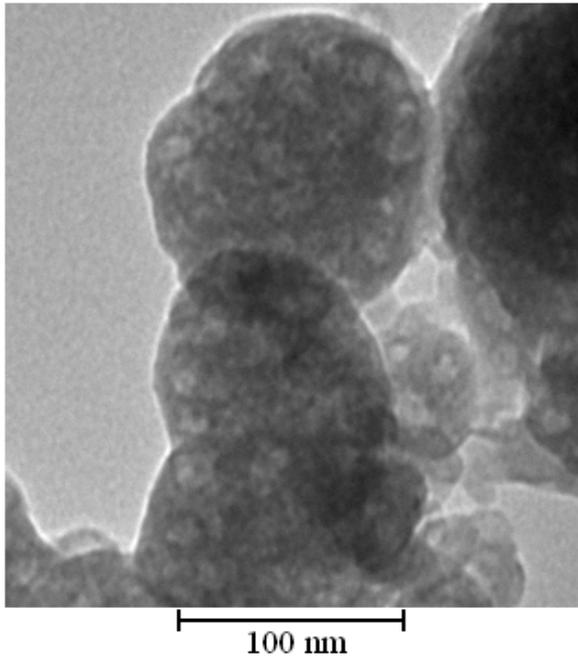


Figure 1: TEM image of clusters from GaP nanoparticles, obtained by aqueous synthesis.

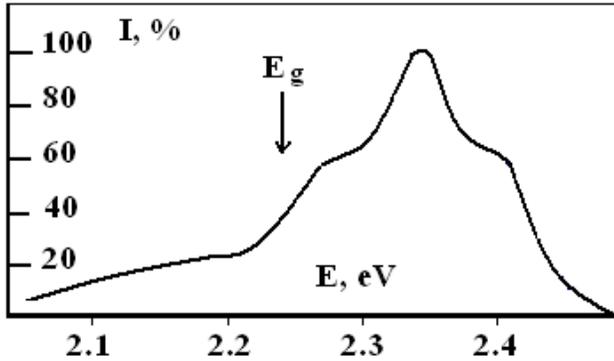


Figure 2: Luminescence of GaP nanoparticles with the dimensions of the order of 10 nm. Luminescence is observed at room temperature; compared with bulk crystals its maximum is shifted to high energies of photons (E_g is the position of the forbidden gap at 300K)

In **Figure 3** one can see a considerable evolution of Raman spectrum of the nanoparticles compared with the bulk crystals. Instead of transversal TO and longitudinal LO lattice phonons of bulk GaP at 365 and 402 cm^{-1} respectively (see the curve 1 in **Figure 3**) the nanocrystals demonstrate their own weak and considerably shifted phonons. Note that opposite to the initial product of the aqueous synthesis (the curve 2) only thoroughly annealed initial mixture demonstrates clear Raman spectrum (the curve 3).

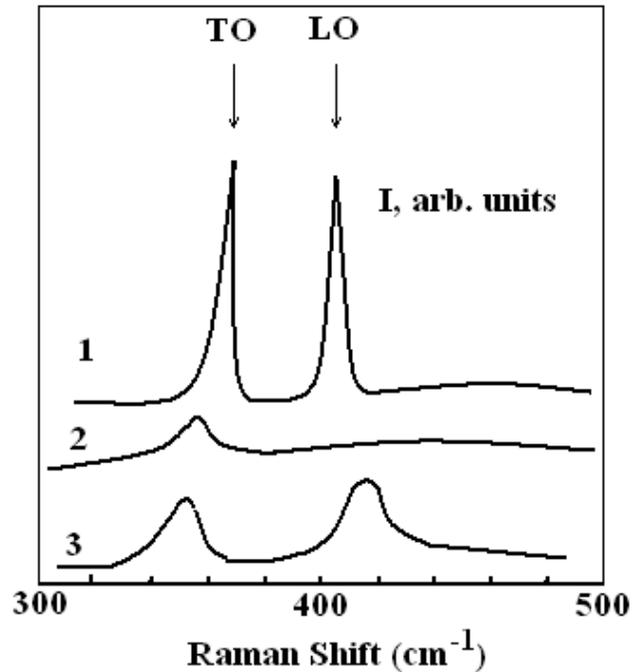


Figure 3: Raman spectra of GaP nanoparticles before (2) and after (3) annealing at Ar flow compared with bulk crystal (1). TO, LO – transversal and longitudinal optical lattice phonons respectively. 300K.

Thus, we demonstrate here that the nanoparticles obtained by a simple aqueous synthesis have the controlled dimensions at which the quantum confinement is clearly observed. In particular, their luminescence is detected at room temperature in the wide spectral region 2.0 – 2.5 eV compared with bulk material where the luminescence is limited on the side of the high energies of photons by the edge of the indirect band gap of GaP (app 2,25 eV at room temperature).

Let us now discuss using the example of GaP some other methods which change the bulk properties of the initial materials like to the the quantum confinement phenomenon or give some additional advantages in the development of nanotechnology.

2.2 Some Properties of Perfect Bulk GaP Crystals

This work also continues the monitoring of properties of GaP single crystals grown 40 years ago [17]. During 2005 - 2006 we investigate their luminescent properties in comparison with the data obtained in 60th, 70th, 80th and 90th of the past century [6, 7, 18 - 20]. Note that due to a lot of defects and a highly intensive non-radiative recombination of non-equilibrium current carriers, initially the luminescence of fresh undoped crystals could be observed only at the temperatures 80K and below. Now luminescence is clearly detected in the region from 2.0 eV

and until 3.0 eV at room temperature (see **Figure 4**, curve 1). Taking into account that the indirect forbidden gap is only 2.25 eV we suppose that this considerable extension of the region of luminescence to the high energy side of the spectrum is connected with a very small concentration of defects, considerable improvement of crystal lattice, high transparency of perfect crystals, low probability of phonon emission at rather high temperature and participation of direct band-to-band electron transitions. The luminescence at 80K has the excitonic band localized at the position of the forbidden band edge (curve 2).

More detailed analyses and discussion of these results will be carried out in the future papers.

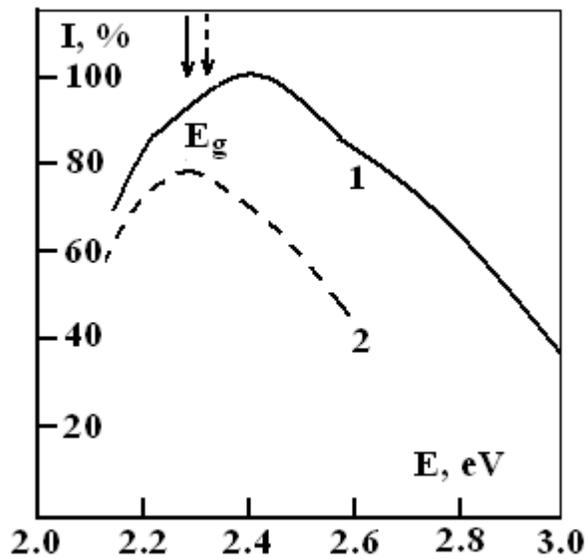
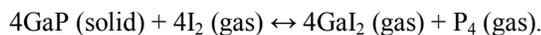


Figure 4: Luminescence of perfect bulk GaP single crystals prepared in 1966 and measured in 2006. Luminescence is observed at room temperature and its maximum is shifted to high energies of photons. The position of the forbidden gap E_g at 300K and 80K is marked by arrows, dotted arrow – 80K

2.3 Chemical Gas Transport Reactions

Chemical transport reactions lead to creation of intermediate gasiform products which can be used as carriers of the necessary substance between two zones of reactions having different temperatures. For GaP [6] the most simple and efficient reaction is:



Crystal growth from gas phase goes spontaneously (so called mass crystallization) or it can be organized from the centers with an ordered structure of their disposition along the area of growth of nano crystals. It is a modification of the method of “cold finger”. The “cold finger” creates a small point on the surface of a substrate with the temperature which is a little bit less than in the vicinity of

this point. The nanocrystals in this case will be fixed exactly on the system of these cold points giving additional opportunities for elaboration of device structures using a specific design of the systems of nanoparticles.

2.4 Laser Assisted Deposition

From the material of a target in this method (the experimental set-up is shown in **Figure 5**) we can obtain 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 before the substrate with the particles of the target and then to deposit again this mixture onto the substrate. Growing pulse by pulse of laser irradiation nano layer 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. **Figure 6 a and b** illustrates this by *in situ* measurement of spectral intensity of the plasma components (a) and *ex situ* analyses of the chemical composition of the nanolayer with a secondary ion mass-spectrometer (b).

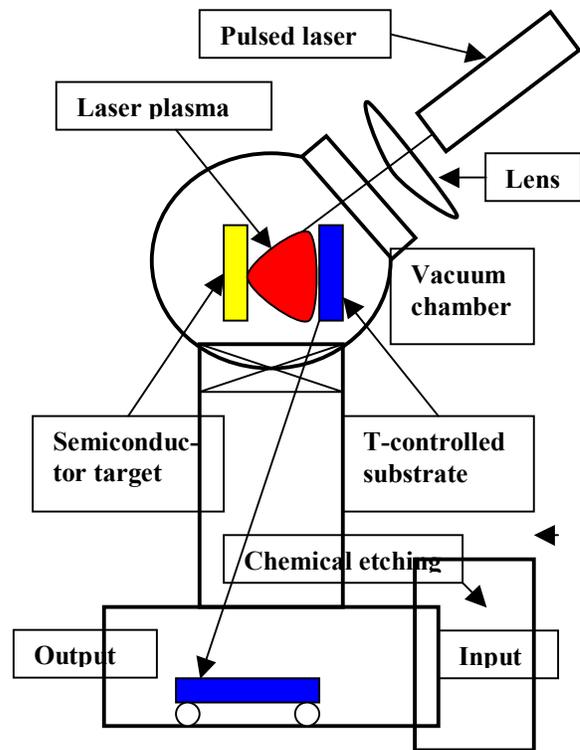


Figure 5: Experimental set-up for laser assisted growth of nanolayers with variable composition. Thickness and quality of the layer is controlled by energy, duration and quantity of laser pulses evaporating a semiconductor target in ultra-high vacuum chamber.

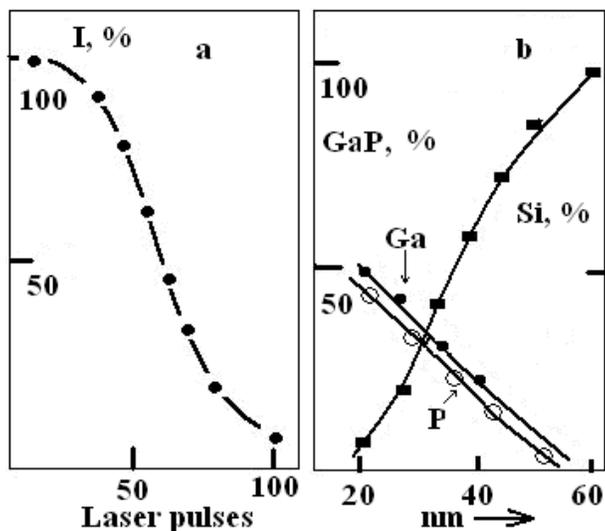


Figure 6a: Spectral intensity of a Na^+ line in vicinity of NaCl substrate during laser assisted deposition of GaP onto it. The creating continuous row of non-equilibrium solid solutions NaCl-GaP changes its concentration from 0 up to 100% of GaP after app. 100 laser shots.

Fig. 6b: The growth of nano layer on the base of GaP-Si solid solution during laser assisted deposition of GaP onto Si substrate. GaP concentration smoothly decreases from 100% on the surface up to 0 in 50 nm depth.

Nanoparticles of a variable chemical composition can be synthesized, combining properties of the materials of the target and the substrate. We can also smoothly conjugate in a nanolayer different crystal structures, lattice parameters, mechanical and thermal properties of target and substrate materials. It means that there exists a unique opportunity to predict and create necessary properties of nano layers and nano particles growing them from a mixture of very different materials. Note that the change of the substrate temperature gives an opportunity to obtain the epitaxial nanolayers at high temperatures (app. 600°C) or nanoparticles with the controlled dimensions at a fixed thickness of the nano layer at low temperatures of the substrate (80-300K).

Note that the solid bound exciton phase discovered by the author in long-time ordered GaP:N single crystals [7, 20] is absolutely new phenomenon supplying a unique opportunity to get various non-linear optical effects at very low exciting light intensity as well as to develop new generation of optoelectronic devices for accumulation, conversion and transport of light energy. Now on the base of GaP we can grow also a multi-layer structure where the monolayer of N atoms will be incorporated in it each 10 nm, creating a one-dimensional periodic structure of N traps for excitons. Preparation of two dimensional perfect net of N impurities along pure GaP film is rather difficult, but also is possible with the help of ion lithography or atomic force microscope built into a growth chamber. Of course, nowadays this technique is a frontier of our

technological possibilities, but within the next 2-3 years some very important results are likely to be obtained also in this direction.

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