Preparation and Characterization of GaP Colloidal Nanoparticles and Films

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***Abstract* — In this communication, we present results of investigations of the influence of technological conditions upon the properties of GaP nanoparticles produced by using a new precursor as a source of Ga atoms. The obtained nanoparticles were investigated by means of XRD, EDAX, and TEM as well as by means of Raman light scattering and photoluminescence spectroscopy. The sizes of nanoparticles obtained with gallium acetylacetonate as a source of gallium are in the range of 10 – 40 nm according to estimations from TEM analysis. These values correlate with the position of the short-wavelength emission maximum in the photoluminescence spectra. A method of electrophoretic deposition of GaP nanoparticles from colloidal organosol solutions was elaborated. Raman spectra and XRD patterns, as well as optical transmission spectra have been measured for layers of GaP nanoparticles produced by this method.**

***Index Terms* — GaP, nanoparticles; electrophoretic deposition; spectroscopy.**

I. INTRODUCTION

Gallium phosphide is an important semiconductor material with wide indirect-band-gap and potential applications for the ultraviolet, blue and blue-green spectral range for optoelectronic and light emissive devices in spectral range from 250 to 500 nm [1,2]. While bulk and thin film GaP has been successfully commercialized for many years, application of its nanocrystals in nanocomposites as a new optical medium has only received attention recently [3-5].

Semiconductor colloidal nanocrystals (NCs) are wet chemically grown nano-objects whose optical and electronic properties are strongly governed by their quality, dimensions and quantum-confinement effects [3]. This work has been fulfilled in framework of the STCU (www.stcu.int) 4610 Project "Advanced Light Emissive Device Structures" and continue our efforts, discussed at the 2006, 2010 and 2011 NSTI Nanotech Conferences [6-8], 2007-2011 TMS Annual Meetings, Conferences and Symposia [9], and published in the relevant books, proceedings and papers [3-10] with the focus being to advance the quality and light emissive properties of GaP nanocomposites and using our new results in preparation of close to ideal bulk GaP single crystals, different methods of GaP nanoparticles syntheses and the most optically and mechanically compatible polymers.

Several methods such as aqueous synthesis of monodispersed GaP nanocrystals, hydrothermal synthesis by the reaction of white phosphorus with gallium metal in benzene [6-8] have been reported by us to the synthesis of GaP nanoparticles. In our previous works GaP nanoparticles were synthesized by similar procedures to those utilized in [11] also by direct reaction of anhydrous gallium (III) chloride ($GaCl_3$) and sodium phosphide (Na_3P) in ambience of nitrogen or argon. GaP nanoparticles are produced as a result of interaction between the (dimethylbenzene) $GaCl_3$ dissolved in the toluene and the Na_3P suspension in the solvent. In this work we present a simple solution-phase method for the synthesis of small sizes of colloidal GaP nanoparticles by using a new precursor as a source of Ga atoms, namely the gallium acetylacetonate $Ga[CH_3COOH=C(O\_)CH_3]_3$. GaP nanoparticles produced by this method demonstrate a pronounced quantum confinement effect.

II. RESULTS AND DISCUSSIONS

In our previous work the GaP nanoparticles were prepared as a result of interaction between the $GaCl_3$ dissolved in the toluene (dimethylbenzene) and the Na_3P suspensio in the solvent, as a result of the following reaction:

$$12Na + P_4 = 4Na_3P \quad (1)$$

A round-bottom flask with three necks (Erlenmeyer flask) is placed in oil bath. A thermometer and a cooler were installed on two of these necks, while the third one was used for scavenging with inert gas (argon). 0.138 g of metallic sodium (6 mmol) and 0.062 g of white phosphorus (2 mmol) are added to 20 ml of toluene. The obtained mixture is maintained at 105°C for 2 hours under intense agitation. As a result a black substance of Na_3P is obtained.

GaP nanoparticles are formed according to the following reaction:

$GaCl_3+Na_3P \rightarrow GaP$ (nanoparticles) $+3NaCl$ (2)

In this communication, we present results of investigations of the influence of technological conditions upon the properties of GaP nanoparticles produced by using a new precursor as a source of Ga atoms, namely the gallium acetylacetonate (Ga $[CH_3COOH=C(O\_)CH_3]_3$). Initially a Na_3P is produced as a result of a direct reaction of the sodium with the white phosphorus in the toluene solution in an inert medium as described by reaction (1). Separately, 0.37 g of gallium acetylacetonate (1 mmol) are dissolved in 15 mL of toluene. The solution of gallium acetilacetonate in toluene is stirred and heated to 110°C. Afterwards, the solution of sodium phosphide in toluene is added to the solution of gallium acetilacetonate and the mixture is heated at this temperature with intensive stirring for 3 h. 0.38 g (1 mmol) of trioctylphosphine oxide (TOPO) is added to the solution as a stabilizer 5 – 10 minutes after the beginning of the syntheses process in order to avoid the agglomeration of particles. The obtained mixture is maintained at 105°C for 4 hour under intense agitation. The formation of GaP nanoparticles occurs according to the following reaction:

$Ga[CH_3COOH = C(O-)CH_3]_3 + Na_3P =$

$= GaP + 3\ Na[CH_3COOH=C(O-)CH_3]$ (3)

Secondary products of the reaction were sedimented in the reactor 12 hours later, and the solution becomes yellow-orange. GaP nanoparticles are segregated from this solution by means of adding dimethylformamide and spinning at 5000 rpm. The influence of the Ga:P ratio in the synthesis process was investigated. It was found that the optimum Ga:P ratio is 2:1.

A method of electrophoretic deposition of GaP nanoparticles from colloidal organosol solutions was elaborated. Electrophoretic deposition was performed in a specially designed cell with glass electrodes covered by an ITO layer as cathode, and with an anode paced 10 mm from the cathode in a fluoroplastic vessel filled with organosol. The organosol was prepared by ultrasound dispersion of preliminarily prepared GaP nanocrystals in a mixture on non-polar solvents. The layers were deposited during 5 – 30 minutes with an applied voltage of 300 – 500 V. The obtained GaP layers have a color from light brown to dark brown characteristic for GaP single crystals.

GaP nanoparticles were investigated by means of Raman scattering, X-ray Diffraction (XRD), Selected Area Electron Diffraction (SAED), Energy Dispersive X-Ray Analysis (EDAX), Transmission Electron Microscopy (TEM) and photoluminescence spectroscopy (PL) under the excitation with the 325 nm line of a He-Cd laser.

Raman spectra of GaP films presented in Figure 1 contain a line due to the transversal optic (TO) phonon at 366.5 cm^{-1} and another line at 403 nm related to the longitudinal optic (LO) phonon. The position of these lines is close to the one characteristic for bulk and GaP nanocrystals [12]. Similarly to bulk crystals, the TO Raman mode of the GaP film 1 exhibits an anomalous asymmetric lineshape due to a Fermi resonance with the two phonon density of states [12-14], while a new band emerges at 362 cm^{-1} in spectra of films 2 and 3. Apart from that, a shoulder emerges in the spectra of films in the low frequency region of the LO band which is usually attributed to surface-related Froehlich mode scattering in GaP nanostructures [15].

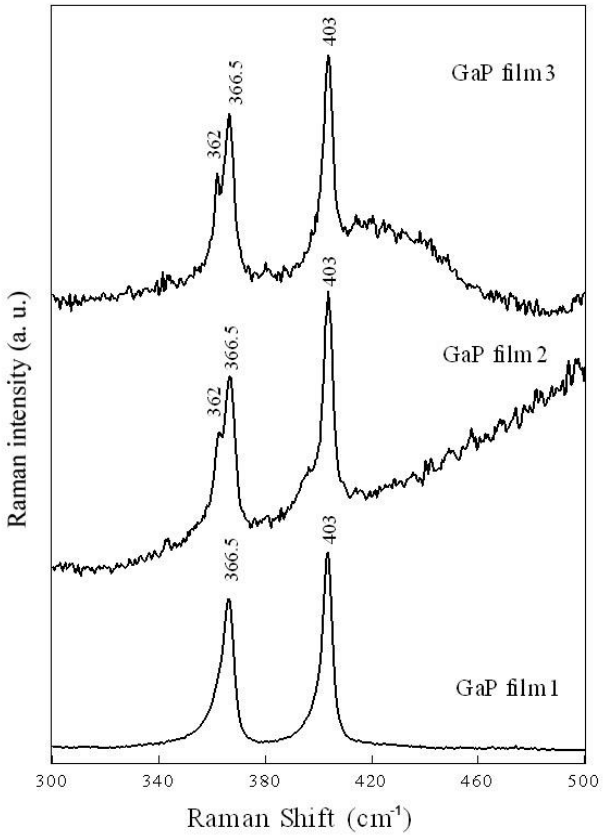

Fig. 1. Raman spectra of GaP films prepared in different technological processes.

According to XRD data (Figure 2) the following reflexes are present in spectra: 28° - (111) plane, 36° - (200) plane, 57° – (311) plane. The other peaks at 32, 46 and 57 are indexed as the (200), (220) and (311) reflections, respectively.

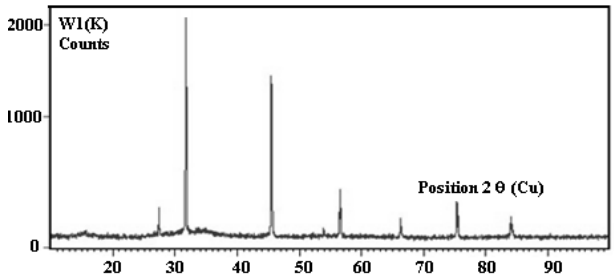

Fig. 2. XRD pattern for GaP nanoparticles.

The uniform GaP nanoparticles having after ultrasonic and other treatments are shown to exhibit improved quality in their suspension and brightness of luminescence at room temperature which is found to be broad band with maximum at 3 eV. Figure 3 presents the photoluminescence spectra of GaP nanoparticles obtained by the above described method for different Na_3P concentrations. Two emission bands at 410 – 420 nm and 640 – 670 nm are observed in the emission spectra. The first emission band is due to radiative recombination in nanoparticles with different sizes, while the second band is due to impurities. A shoulder at 380 nm is also

observed in the spectra which correspond to nanoparticles size of ~ 3-4 nm [16].

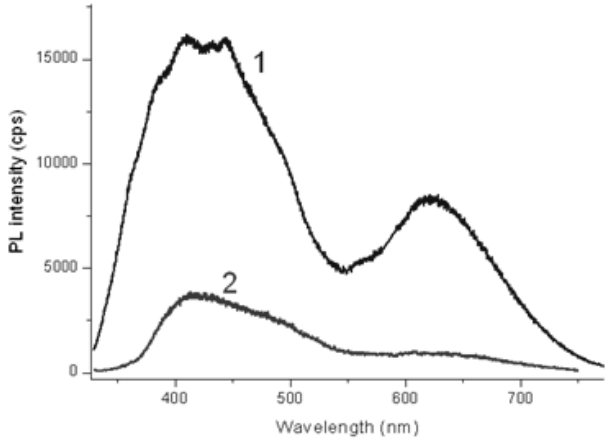

Fig. 3 Photoluminescence spectra for GaP nanoparticles under excitation of He-Cd laser. T=300K. 1 – 0.002 mol Na_3P; 2 – 0.003 mol Na_3P.

The sizes of nanoparticles obtained with gallium acetylacetonate as a source of gallium are in the range of 10 – 40 nm according to estimations from TEM analysis (Figure 4). These values correlate with the position of the short-wavelength emission maximum in the photoluminescence spectra. It is know that the bulk GaP is an indirect semiconductor with an indirect band gap of 2.22 eV (559 nm) and a direct band gap of 2.78 eV (446 nm) at room temperature. The shoulder at 380 nm can be attributed to the direct transitions, while the maximum of emission at the 480 nm is due to indirect transitions in the GaP nanoparticles. It is evident that a shift of both the direct (0.48 eV) and indirect (0.38 eV) band gap occurs in nanoparticles as compared to the bulk GaP.

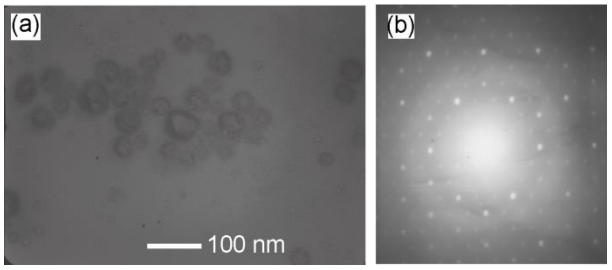

Fig. 4. A representative TEM image of GaP nanoparticles (a) with corresponding SAED pattern.

In order to explain this interesting phenomenon we postulate that the nanocrystals, much like the ideal long-term ordered bulk GaP single crystals, exhibit this huge increase in blue-shifted luminescence due to: (a) negligibly small influence of defects and non-radiative recombination of electron-hole pairs and very high efficiency of their radiative annihilation, (b) high perfection of nanocrystal lattice, and (d) high transparency of nanocrystals due to their small dimensions for the light emitted from high points of the GaP Brillouin zones, for instance, in the direct transitions Γ_1^c - Γ_{15}^v between conductive and valence bands with the photon energy at 300K equal to 2.8 eV [17] and (e) high efficiency of this so called "hot" luminescence. Note, that the thoroughly prepared nanocomposites on the base of the suspensions containing only app. the 10 nm nanoparticles, also exhibit bright luminescence with maximum at 3.2 eV due to high transparency of 10 nm nanoparticles for these high energy emitted photons and pronounced quantum confinement effects since this diameter equals the Bohr diameter of the bound exciton in GaP [18].

The TEM data confirm that the proposed technological method allows one to significantly reduce the size of GaP nanoparticles to 8 – 40 nm. The SAED image is indicative of crystalline nanoparticles, showing spot patterns. It is obvious that there appear three sets of diffraction patterns, and the diffraction rings can be indexed to (111), (220), and (311) planes of zinc-blende GaP structure.

III. CONCLUSIONS

Our first attempts to prepare GaP nanoparticles [6] yielded room temperature luminescence with maximum shifted only to 2.4 eV in comparison with the new maximum at 3.2 eV. Currently prepared nanocrystals of about 10 nm sizes, thoroughly separated and distributed in a suspension, that prevent their coagulation, mechanical and optical interaction, have bright broad-band luminescence with the position of maximum , which, dependently on the ratio of nanoparticles with different dimensions in their mixture or nanocomposites, can be changed from the edge of the forbidden gap until 3.2 eV, approximately 1 eV far from the position of the absorption edge in GaP at 300^{o}K. The GaP nanoparticles prepared by colloidal low temperature method using gallium acetylacetonat as a precursor of gallium atoms and temperature treatment can be used to improve the quality of nano-suspension. A uniform fraction of nanoparticles of about 8-10 nm in diameter is produced by using gallium acetylacetonate ($Ga[CH_3COOH=C(O-)CH_3]_3$) as source of gallium atoms. These nanoparticles as the best nanoparticles prepared by us using the other methods[2-10] show an intense luminescence band with the maximum at 3.2 eV determined by quantum-confinement effect and high transparency of the nano-sized particles.

Our results on luminescence of GaP nanoparticles and GaP/polymers nanocomposites confirm significant achievements in technologies of their preparation. On the base of these improved technologies we can change within the broad limits the main parameters of luminescence and expect to create a framework for novel light emissive device structures using dramatic 1 eV expansion of GaP luminescence to UV region.

Comparing the results on X-ray diffraction, Raman light scattering, microscopy of high resolution and luminescence obtained on GaP freshly grown and long-term ordered bulk single crystals, nanoparticles and their nanocomposites, prepared by us using different approaches and methods, described in [2-10], we confirm a big similarity in properties of the perfect GaP bulk single crystals and their best nanoparticles, wide opportunities for their preparation using the known nanotechnology methods, a good compatibility of GaP nanoparticles with different polymer matrix for

fabrication of nanocomposites as well as very interesting and important for application in optoelectronics possibilities to change in wide extent from infrared to ultraviolet width and position of maximum of the luminescence band.

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