

Fabrication and Characterization of the GaP/Polymer Nanocomposites for Advanced Light Emissive Device Structures

S.L. Pyshkin^{*}, J. Ballato^{**}, I. Luzinov^{***}, and B. Zdyrko^{***}

^{*} Adjunct Professor of Clemson University, SC, permanent address: Institute of Applied Physics, Academy of Sciences, Academy St. 5, MD2028, Kishinev, Moldova, spyshkin@yahoo.com

^{**} Center for Optical Materials Science & Engineering Technologies (COMSET), Clemson University, Technology Dr. 91, Anderson, SC 29625, USA, jballat@clemson.edu

^{***} School of Materials Science and Engineering and Center for Optical Materials Science and Engineering Technologies, 161 Sistine Hall, Clemson University, Clemson, SC 29634, USA, LUZINOV@exchange.clemson.edu, BOGDANZ@exchange.clemson.edu

ABSTRACT

Nanoparticles of GaP have been prepared using yellow P and a mild aqueous low temperature synthesis followed by ultrasonication. The resulting nanocomposites yielded a bright luminescence at room temperature in a broad band with the maximum ranging between 2.5-3.2 eV and showing pronounced quantum confinement effects.

Using an improved technology for the preparation of GaP nanoparticles and methods for fabricating GaP/polymer nanocomposites we expect to create a framework for novel light emissive device structures.

Keywords: Light emissive GaP/polymer nanocomposites

1 INTRODUCTION

This work continues our efforts to advance GaP/polymer nanocomposites for light emissive devices based on GaP nanoparticles. The components of these nanocomposites demonstrate complementary behavior and each is a candidate for use in light emitters, waveguides, converters, accumulators and other planar, fiber or discrete micro-optic elements. While bulk and thin GaP films have been successfully commercialized for many years, its application in device nanocomposite structures for accumulation, conversion and transport of light energy has only received attention recently.

Nanoparticles of GaP have been prepared on the basis of yellow P using mild aqueous low temperature synthesis [1]. The spectra of photoluminescence (PL) and Raman light scattering (RLS), X-ray diffraction (XRD) and electron microscopy (TEM) of the nanoparticles prepared under different conditions have been compared with each other as well as with those from bulk single crystals. After the relevant investigation of different regimes and components for hydrothermal reactions this type of the synthesis has been chosen as an optimal one. In preparation of the nanocomposite we used the fractions of uniform GaP nanoparticles having after a thorough ultrasonic treatment and a number of other operations improving the quality of the nano-suspension a bright luminescence at room

temperature in a broad band with the maximum, dependently on the concrete synthesis conditions, between 2.4 – 3.2 eV, while the value of the forbidden gap in GaP at room temperature is only 2.24 eV. Note that according to our investigations of these conditions and data on nanoparticles characterization, only a combination of low temperature synthesis, using yellow P and thorough ultrasound treatment of the reaction products leads to the maximum broad band and UV shift of luminescence.

This paper and a companion paper [1] discuss light emissive sources on the base of transparent robust fluoropolymer and GaP nanoparticles.

2 EXPERIMENTAL PROCEDURE AND DISCUSSION

The details of preparation by mild aqueous synthesis [1, 3] suitable for light emissive nanocomposites GaP nanoparticles as well as the influence of different temperatures, modifications and compositions of the reacting components on quality of the particles can be found in [1].

The dried powders were characterized using standard methods of XRD, TEM, Raman scattering and photoluminescence. For comparison we used also industrial and specially grown and aged GaP single crystals [1-11]. Polyglycidyl methacrylate (PGMA), polyglycidyl methacrylate-co-polyoligoethyleneglycol methacrylate (PGMA-co-POEGMA) and biphenyl vinyl ether (BPVE) polymers were used for preparation on GaP nanocomposites. Thickness of the polymer composite film was within 250-300 nm defined from AFM scratch experiment. The next procedures have been used in fabrication of the nanocomposites:

1) GaP powder was ultrasonicated in methylethylketone (MEK) using Branson 5210 ultrasonic bath. Then, PGMA was added to the MEK solution. GaP to polymer ratio was less than 1:10. Films were deposited via dip-coating;

2) GaP powder was dispersed in water-ethanol mixture (1:1 volume ratio) and ultrasonicated using Branson 5210 bath for 120 min. Then, polyglycidyl methacrylate-co-polyoligoethyleneglycol methacrylate (PGMA-co-

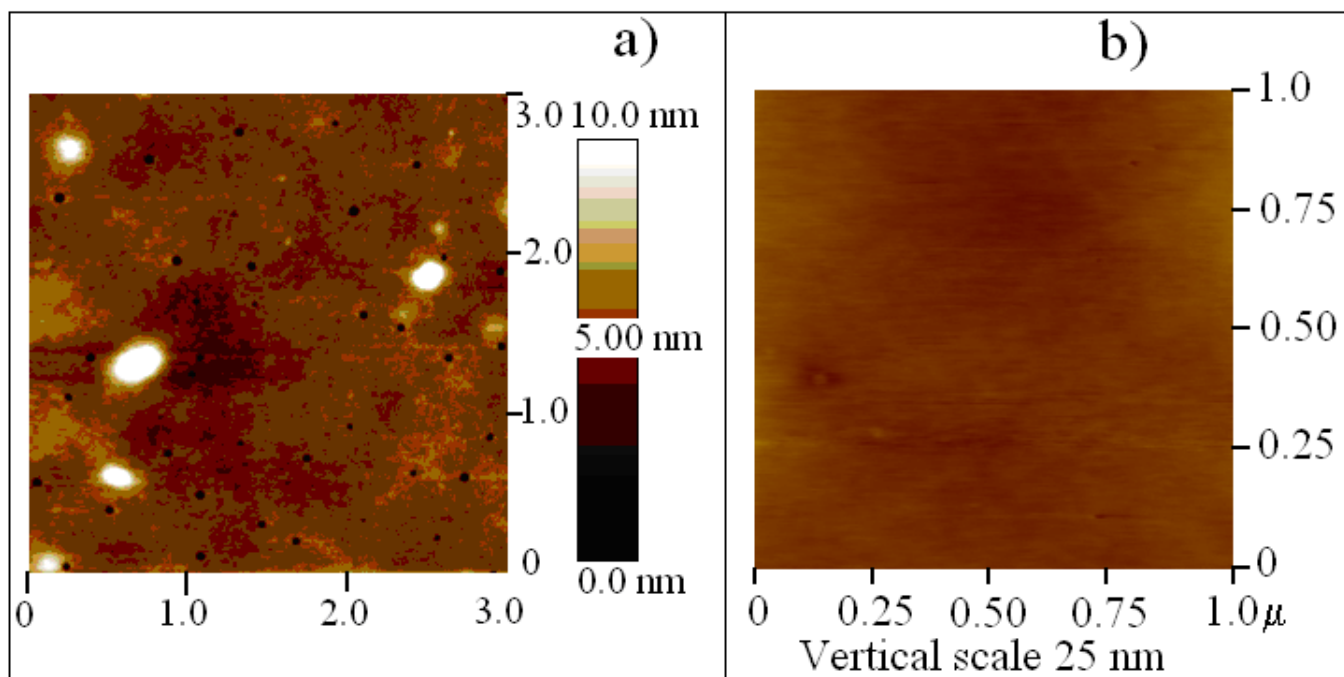


Figure 1 : AFM topography images of the GaP/PGMA (Fig. 1a) and GaP/ PGMA-co-POEGMA (Fig. 1b) nanocomposites.

POEGMA) was added in form of water-ethanol mixture (1:1 volume ratio) solution. GaP to polymer ratio was less than 1:3. Films were deposited on quartz slides via dip-coating;

3) GaP powder was dispersed in the biphenyl vinyl ether/dichloromethane (BPVE/DCM) solution, then the solution was stirred and filtered from the excess of the powder. A few mL drops of the settled solution were casted onto silicon wafer.

Surface morphology of the films was studied with AFM. AFM was performed on a Dimension 3100 (Digital Instruments, Inc.) microscope. We used the tapping mode to study the surface morphology of the composite films in ambient air.

Luminescence of the nanocomposites was excited by the N₂ laser nanosecond pulses at wavelength 337 nm and measured at room temperature.

Figure 1 shows the AFM topography images of the GaP/PGMA (Fig. 1a) and GaP/ PGMA-co-POEGMA (Fig. 1b) nanocomposites. Note that thoroughly washed, ultrasonicated and dried nanopowder obtained by mild low temperature aqueous synthesis from yellow P may be used for fabrication of quite good blue light emissive nanocomposites (**Fig. 1a** and **Fig. 2, spectrum 2**), but the best quality can be obtained only in fabrication of the nanocomposite from similarly prepared nanoparticles, but stored as a suspension in a suitable liquid (**Fig. 1b** and **Fig. 2, spectrum 1**).

Figure 2 shows spectra of luminescence from GaP/ PGMA-co-POEGMA nanocomposites. GaP nanoparticles have been prepared using yellow P by mild aqueous synthesis at decreased temperature, stored as the suspension

in a liquid (**spectrum 1**) or the dry powder (**spectrum 2**).

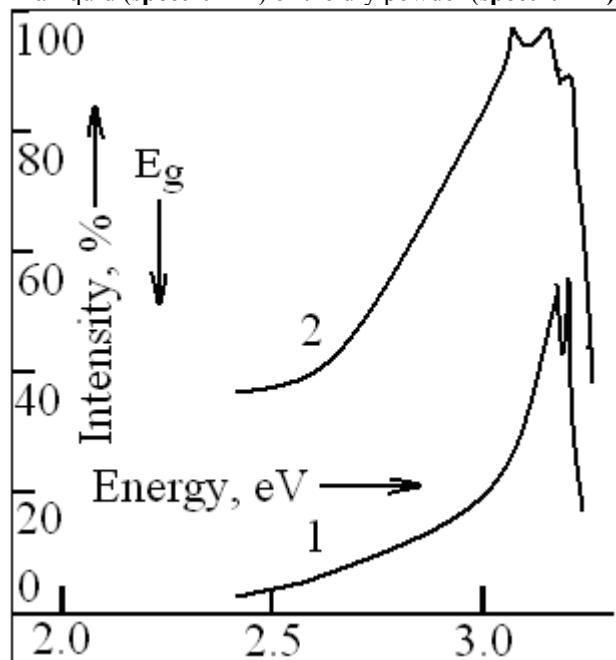


Figure 2 : Spectra of luminescence from GaP/ PGMA-co-POEGMA nanocomposites. GaP nanoparticles have been prepared using yellow P by mild aqueous synthesis at decreased or temperature and stored as the suspension in a liquid (**spectrum 1**) or the dry powder (**spectrum 2**).

The maximum UV shift of the luminescence, app. 1 eV has the nanocomposite prepared on the base of the suspension

(**spectrum 1**), so, one can assume that the mostly uniform and small high quality nanoparticles with pronounced quantum confinement effect are stored in the suspension.

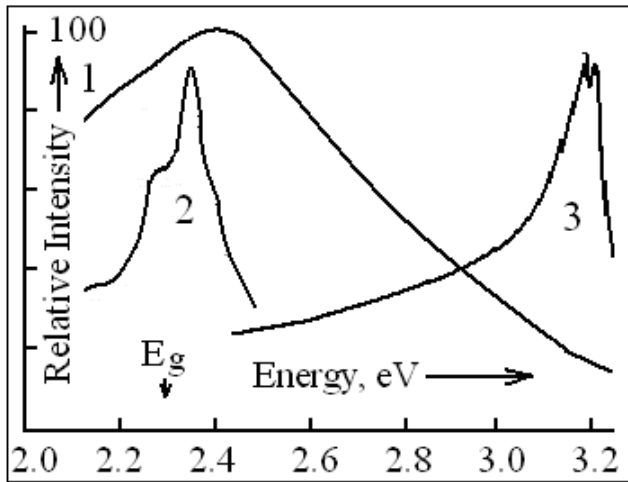


Figure 3 : Luminescence spectra from perfect, long-term ordered GaP single crystals (1) in comparison with the spectra of GaP nanoparticles and nanocomposites, prepared in 2005 – 2006 (2) and now (3).

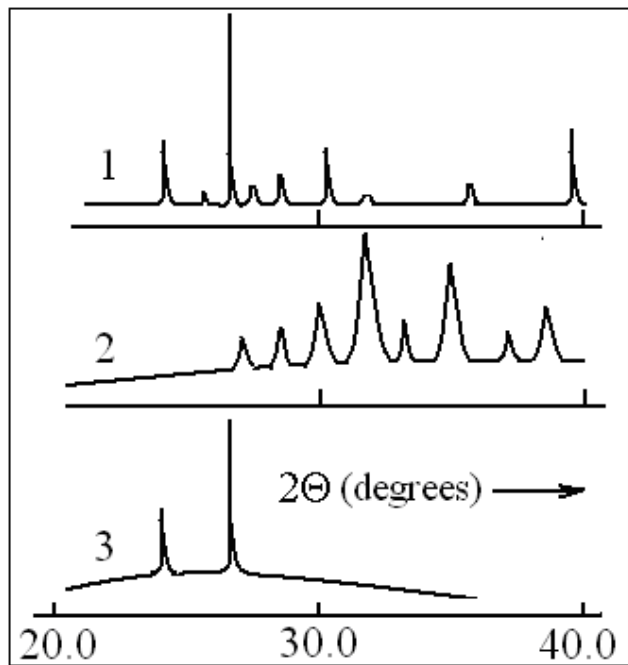


Figure 4: X-ray diffraction from GaP nanoparticles of the best to the moment performance (**spectrum 1**) in comparison with the diffraction from not thorough prepared GaP nanoparticles and perfect GaP bulk single crystal (**spectra 2 and 3 relatively**).

Figure 3 presents the luminescence spectra of our perfect, long-term (up to 50 years) ordered GaP single crystals in comparison with the spectra of GaP

nanoparticles and nanocomposites, prepared in 2005 – 2006 and now. As we note earlier [3, 6, 8, 11], the luminescence was absent at room temperature in newly-made industrial and in our freshly prepared crystals, but it was bright in the same our 40 years aged crystals and shifted to UV up to 2.4 eV at the 2.24 eV forbidden gap for GaP bulk single crystals (**Fig. 3, spectrum 1**). Our first attempts to prepare GaP nanoparticles, dated by the years 2005-2006 [3], gave their room temperature luminescence with maximum shifted only to 2.4 eV (**Fig. 3, spectrum 2**) that in comparison with the new maximum at 3.2 eV (**Fig. 3, spectrum 2**) confirms serious achievements in technology of GaP nanoparticles and GaP based nanocomposites.

Considerable changes in quality of GaP nanoparticles due to improvement of their preparation are shown in **Figure 4**, where one can see X-ray diffraction from GaP nanoparticles of the best to the moment performance (**spectrum 1**) in comparison with the diffraction from not thorough prepared GaP nanoparticles and perfect GaP bulk single crystal (**Figure 4, spectrum 2 and 3 respectively**). One can see very narrow and intense XRD lines from GaP nanoparticles and bulk single crystals of high quality contrary to broad diffraction lines from not thoroughly prepared GaP nanoparticles (**spectra 1, 3 contrary to spectrum 2**).

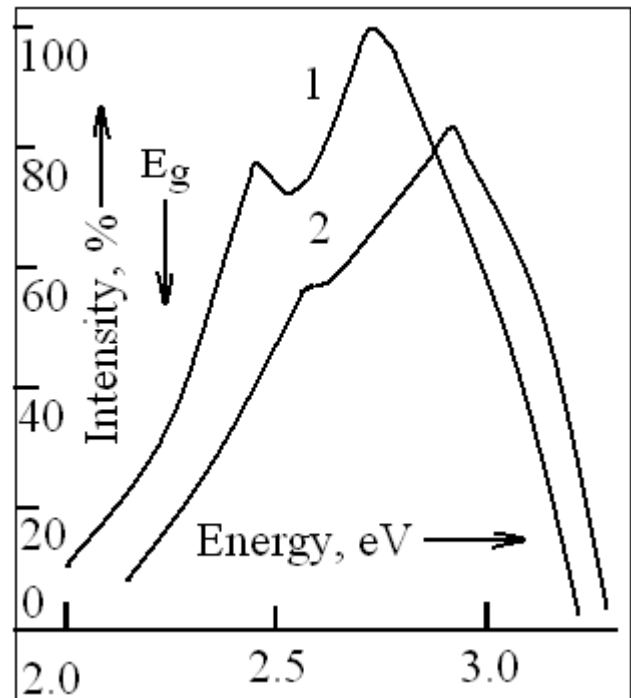


Figure 5 : Luminescence spectra of 2 GaP/BPVE nanocomposites produced on the base of 2 parties of GaP nanoparticles prepared using different conditions.

Recently we started investigation of the GaP/BPVE nanocomposite as a prospective light emissive device structure. **Figure 5** shows the luminescence spectra of 2

nanocomposites produced on the base of 2 parties of GaP nanoparticles obtained under different conditions (temperature, modification of P, etc.). The details and results of this work will be published in the nearest future.

In this paper we note that in the GaP/BPVE nanocomposite the position of the luminescent maximum can be changed between 2.5 – 3.2 eV and the brightness is 20-30 more than in the PGMA and PGMA-co-POEGMA matrixes.

3 CONCLUSIONS

Using an improved technology for preparation of GaP nanoparticles and methods of fabrication of the GaP/polymer nanocomposites we can change within the broad limits the main parameters of luminescence.

ACKNOWLEDGEMENTS

The authors are very grateful to the US Dept. of State, Institute of International Exchange, Washington, DC, the US Air Force Office for Scientific Research, Science & Technology Center in Ukraine (STCU), Clemson University, SC, Istituto di elettronica dello stato solido, CNR, Rome, Italy, Università degli studi, Cagliari, Italy, Joffe Physico-Technical Institute, St. Petersburg State Technical University, Russia and Academy of Sciences of Moldova for support and attention to our extended (1963-2009) research efforts.

Our special gratitude to Dr. E. Rusu and Dr. N. Tsyntsaru from Institute of Electronic Engineering and Industrial Technologies, Dr. A. Siminel, post graduate students S. Bilevschii and A. Racu from Institute of Applied Physics, Moldova, Dr. D. Van DerVeer, Clemson University, for their contribution in elaboration of GaP nanotechnology, characterization of nanoparticles and nanocomposites.

REFERENCES

- [1] S.L. Pyshkin, J. Ballato, G. Chumanov, N. Tsyntsaru and E. Rusu, "Preparation and Characterization of Nanocrystalline GaP for Advanced Light Emissive Device Structures", will be published in Proceedings of the Nanotech Conference and Expo 2010, June 21-25, Anaheim, CA
- [2] S. Pyshkin, J. Ballato, M. Bass, G. Chumanov and G. Turri, "Properties of the Long-term Ordered Semiconductors", The 2009 TMS Annual Meeting and Exhibition, San Francisco, Feb 15-19, Suppl. Proc., Vol. 3, pp 477-484.
- [3] S.L. Pyshkin, J. Ballato, G. Chumanov, J. DiMaio and A.K. Saha, "Preparation and Characterization of Nanocrystalline GaP", Symposium "Nanoelectronics and Photonics", 2006 NSTI Nanotech Conference,

- Boston, May 7-11, Technical Proceedings of the Conference, Vol. 3, pp 194-197
- [4] S.L. Pyshkin, J. Ballato, G. Chumanov, "Raman light scattering from long-term ordered GaP single crystals", J. Opt. A: Pure Appl. Opt. **9** (2007) 33–36, IOP Publ. House, London
- [5] S.L. Pyshkin, J. Ballato, M. Bass, G. Turri, "Luminescence of Long-Term Ordered Pure and Doped Gallium Phosphide", (*invited*) Symposium "Recent Developments in Semiconductor, Electro Optic and Radio Frequency Materials", TMS 2007 Annual Meeting & Exhibition, Orlando, FL, Feb - March 2007; J. Electronic Materials, Springer, Vol. 37, #4, pp 388-395 (2008)
- [6] S. L. Pyshkin, R. Zhitaru, J. Ballato, "Modification of Crystal Lattice by Impurity Ordering in GaP", Int. Symposium on Defects, Transport and Related Phenomena, Proc. MS & T 2007 Conf., pp 303-310, Sept 16 –20, 2007, Detroit, MI
- [7] S.L. Pyshkin, J. Ballato, M. Bass, G. Turri, (*invited*), "Evolution of Luminescence from Doped Gallium Phosphide over 40 Years", TMS 2008 Annual Meeting, Symposium: Advances in Semiconductor, Electro Optic and Radio Frequency Materials, March 9–13, New Orleans, LA, J. Electron. Mater., Vol. 38, #5, pp 640-646 (2009).
- [8] Sergei L. Pyshkin, John Ballato, Michael Bass, George Chumanov and Giorgio Turri, "Time-dependent evolution of crystal lattice, defects and impurities in CdIn₂S₄ and GaP", The 16th Int Conference on Ternary and Multinary Compounds (ICTMC16), Berlin, Sept 15-19, 2008; Phys. Status Solidi, C 6, No. 5, pp 1112–1115 (2009).
- [9] S. Pyshkin, R. Zhitaru, J. Ballato, G. Chumanov, M. Bass, "Structural Characterization of Long Term Ordered Semiconductors", Proc. of the 2009 MS&T Conference, Pittsburgh, October 24-29, Int. Symposium "Fundamentals & Characterization", Session "Recent Advances in Structural Characterization of Materials", pp 698-709.
- [10] Sergei Pyshkin, John Ballato, Andrea Mura, Marco Marceddu, "Luminescence of the GaP:N Long-Term Ordered Single Crystals", Suppl. Proceedings of the 2010 TMS Annual Meetings (Seattle, WA, USA, February, 2010, vol.3, pp 47-54.
- [11] "Advanced Light Emissive Device Structures", STCU (www.stcu.int) Project 4610, 2009-2012.