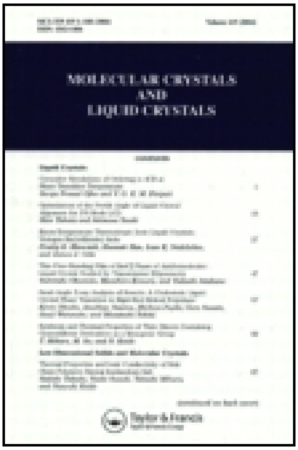

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Electronic Processes in the Porous Silicon-Conducting Polymer Heterostructures

O. Aksimentyeva [a] , L. Monastyrskyi [a] , V. Savchyn [a] , P. Stakhira [b] , Ya. Vertsimakha [c] & B. Tsizh [d]
[a] Ivan Franko Lviv National University, Lviv, Ukraine
[b] National University "Lviv Polytechnics", Lviv, Ukraine
[c] Institute of Physics, NAS of Ukraine, Kyiv, Ukraine
[d] Kazimierz Wielki University, Bydgoszcz, Poland

To cite this article: O. Aksimentyeva, L. Monastyrskyi, V. Savchyn, P. Stakhira, Ya. Vertsimakha & B. Tsizh (2007): Electronic Processes in the Porous Silicon-Conducting Polymer Heterostructures, Molecular Crystals and Liquid Crystals, 467:1, 73-83

To link to this article: http://dx.doi.org/10.1080/15421400701220957

Mol. Cryst. Liq. Cryst., Vol. 467, pp. 73–83, 2007
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400701220957

Electronic Processes in the Porous Silicon-Conducting Polymer Heterostructures

O. Aksimentyeva
L. Monastyrskyi
V. Savchyn
Ivan Franko Lviv National University, Lviv, Ukraine

P. Stakhira
National University “Lviv Polytechnics”, Lviv, Ukraine

Ya. Vertsimakha
Institute of Physics, NAS of Ukraine, Kyiv, Ukraine

B. Tsizh
Kazimierz Wielki University, Bydgoszcz, Poland

The effect of an integrated polymer on the luminescence characteristics of porous silicon (PS)-conducting polymer (CP) heterostructures has been studied. Both n-*(100) and* p-*type (111) PS has been employed in order to prepare the heterostructures. To obtain the integrated polymer layers (polyaniline, polymethoxyaniline, polyphenylacetylene, poly-*para-*phenylene, poly-N-epoxy-propylcarbazol), the methods of electrochemical polymerization, vacuum deposition, and spin coating have been used. The obtained structures were studied using atom force microscopy and were examined as to the capability to photoluminescence (PL) and cathodoluminescence (CL). It has been found that the presence of a CP layer on the PS surface preserves the “red” PL, but weakens it to 50–90%. The CL spectra of the obtained heterostructures allow us to suggest their capability of electroluminescence in the visible region of the spectrum.*

Keywords: cathodoluminescence; conducting polymer; heterostructure; photoluminescence; porous silicon

Address correspondence to O. Aksimentyeva, Chemical Department of Ivan Franko Lviv National University, 6 Kyryla-Mefodia St., Lviv 79005, Ukraine. E-mail: aksimen@org.lviv.net

INTRODUCTION

The methods of fabricating the heterostructures based on inorganic and organic semiconductors have attracted a great attention of researchers due to the prospect of using such structures in solar cells [1,2], light-emitting diodes [3], sensors [4,5], lasers [6], and memory devices [7]. A special place is occupied by the heterogeneous systems based on nano-crystal porous silicon (PS), having a wide application in optoelectronics and sensor devices [8,9]. One of the important properties of such structures is their capability of luminescence in the visible and near IR region of the spectrum, the excitation of which becomes possible due to the quantum-size effects, as a result of the nanometer size of a porous structure [8]. Of great interest are the heterostructures created on the PS and surface organic layers, among which the conjugated conducting polymers, particularly polyaniline (PANI), have been intensively studied [10,11,13].

The thin layer of a conducting polymer (CP) on the porous silicon (PS) surface could serve both as a protective layer and an electrical contact [11,13]. Since the electronic properties of CP significantly depend on the level of oxidation (or protonation), the sensitivity of the formed heterostructures to chemical factors such as pH, humidity, gas absorption, and bioactive substances increases due to this modification. This may be used in the fabrication of sensors [5]. It has been found that PS–CP heterojunctions with a PANI layer show the rectifying current-voltage characteristics [10,13] and a visible photoluminescence (PL) [11]. The formation of a silicon-based structure with controlled electroluminescence (EL) properties remains to be an important and unsolved task, which could serve to the purpose of creating the light-emitting diodes. One of the tests regarding the EL manifestation is the study of cathodoluminescence (CL) spectra, which can be used in studying the n-p transitions in semiconductors without coating with special contacts [14]. Therefore, the present paper studies the effect of an integrated polymer on the photo- and cathode-luminescence characteristics of PS–CP heterostructures. In this connection, the development of effective methods of obtaining the heterostructures based on PS and CP and the investigation of their CL and PL properties turn out to be very urgent.

The aim of the present article is to study the possibility of obtaining the controlled thin conducting polymer layers on the PS surface and to examine the irradiative (emission) properties of the fabricated heterostructures.

EXPERIMENTAL

The surfaces of initial single crystal silicon wafers used were oriented to (111) direction (n-type) and (100) (p-type) with a specific resistance of 4.5 and 6.4 ohm·cm, respectively, and 460 µm of the thickness. The wafer anodization was carried out in a 40% HF solution in ethyl alcohol at a current density of 10 mA·cm^{-2} and under illumination by a 150-W tungsten lamp during 10–20 min according to [10].

In order to integrate the polyaminoarenes {poly-o-methoxyaniline (POMA) and PANI}, the method of electrochemical polymerization with cyclic potential sweeping in 0.1 M solutions of a purified monomer in 0.5 M H_2SO_4 was used. A wafer of PS of 1 cm^2 in area was an operating electrode, a platinum wire was used as a counter electrode, and a saturated Ag/AgCl electrode was employed as a reference one. A potentiostat PI-50 was a power source. After coating the film, the samples were rinsed with deionized water and dried under vacuum at 353–373 K during 4 h. Poly-para-phenylene (PPP) films were obtained by vacuum deposition of the chemically synthesized polymer at a residual pressure of 10^{-6} Torr, the substrate temperature of 373 K, and the sample vaporization temperature $T = 800$–1000 K. The formation of PS-poly-phenyl acetylene (PPA) and PS-poly-epoxy-propylcarbazole (PEPC) heterostructures was carried out by spin coating as described in [2]. The study of the topology of surface layers was carried out using an atom force microscope (Nano Scope IIIa) which allows one to obtain the data on the surface microrelief on the nanometer scale and makes it possible to investigate the samples immediately in air. The results were analyzed using the program support by PSI.

PL was excited by a pulse nitrogen laser LGI-21 ($\lambda = 337.1$ nm), the pulse duration $\tau_p = 20$ ns, at a frequency of 60 Hz. The measurements were carried out both at room temperature and the liquid nitrogen temperature. CL was excited by a pulse electron beam with the energy $E\text{p} = 9$ keV, pulse frequency $f = 50$ Hz, and $\tau_p = 3$ µs. The current density in the electron beam $j = 150$ A/m^2. The temperature of CL measurements was 80 K.

RESULTS AND DISCUSSION

The CP layer on the PS surface is obtained in most cases by spin-coating from a polymer solution [5]. However, in such cases, the penetration of polymer molecules to the pores of silicon is not satisfactory even after the ultrasound treatment. It is expected that, under conditions of electrochemical polymerization, when a polymer is formed directly on the electrode surface, the polymer integration may proceed inside the porous silicon layer. To develop the electrochemical method of fabrication of a porous silicon-polymer heterostructure, the cyclic volt-ampere curves (CVA) of PS samples in a monomer and a blank solution (0.5 M H_2SO_4) have been studied (Fig. 1).

A proportional relation between the anode peak current in the interval $E = 0.4$–$0.6\,V$ and the cycle number in the interval $N = 4\ldots16$ makes it possible to control the process of electroactive film formation on the PS surface using the known relationship between the peak current and the film thickness [15]. The heterostructures PS−CP obtained after potential scanning ($N = 12$–15) exhibit a high electrochemical activity, which is another evidence for the formation of a polymer film on the PS surface.

To study the character of surface layers, the topology of obtained heterostructures has been determined by means of atom-force microscopy (AFM). The surface of PS has the shape of vertical nanorods created due to the etching of separate places of the single silicon surface. As a result of statistical analysis of AFM-images, it was defined that the pore depth achieves 200 nm at the total thickness of a porous layer of about 5 μm.

The PAN films obtained on the surface of PS repeat, in general, the relief of the surface forming a continuous polymer layer. However, the morphology of the film is difficult to be interpreted due to the

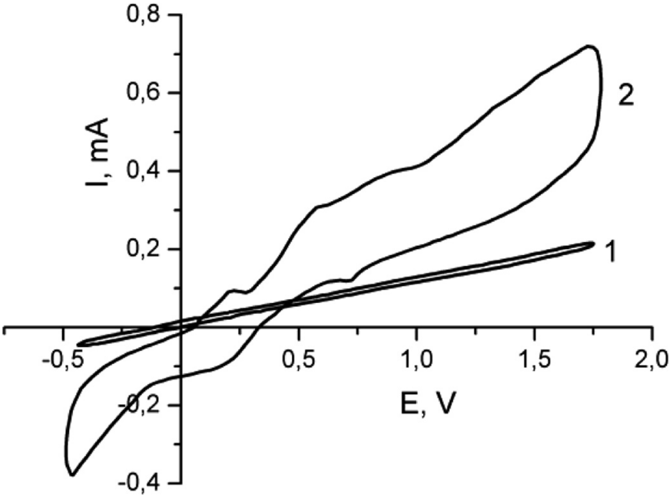

FIGURE 1 Cyclic volt-ampere curves of the n-PS (1) and n-PS–PANI (2) heterostructures in a 0.5 M H_2SO_4 aqueous solution at the potential sweep rate of 80 mV/s.

irregularity of the PS surface. The AFM image for a PAN film obtained under similar conditions on the surface of single crystal silicon (Fig. 2) confirms a globular structure of the obtained film. The polymer layer thickness is about 125 nm.

The PS−PANI and PS−POMA heterostructures fabricated by means of potential scanning ($N = 12$) exhibit not only an increasing electrochemical activity (Fig. 1), but also an increased sensitivity of current-voltage characteristics (VAC) to the illumination [13]. The dependence of VAC and PL on gas absorption [5] may be associated to the processes of film reduction, which causes the increase of the resistance and the optical transmittance of the heterojunction.

Spectra of PL are studied in the spectral range of 1.5–3.1 eV. As seen in Figure 3, the obtained PL spectra are in good agreement with the ones described for PS in theliterature [10,11].

For PS formed on the surface of silicon (100) with the *n*-type of conductivity, the PL spectrum is a band with clear maximum at 1.95 eV. For PS (111) of the *n*-type conductivity, two PL maxima are observed at 2.05 and 2.12 eV. The spectrum disintegration into Gaussian components makes it possible to separate another PL maximum at 2.21 eV.

According to the contemporary ideas, the appearance of PL in PS in the visible range of the spectrum is caused by the quantum-size effect

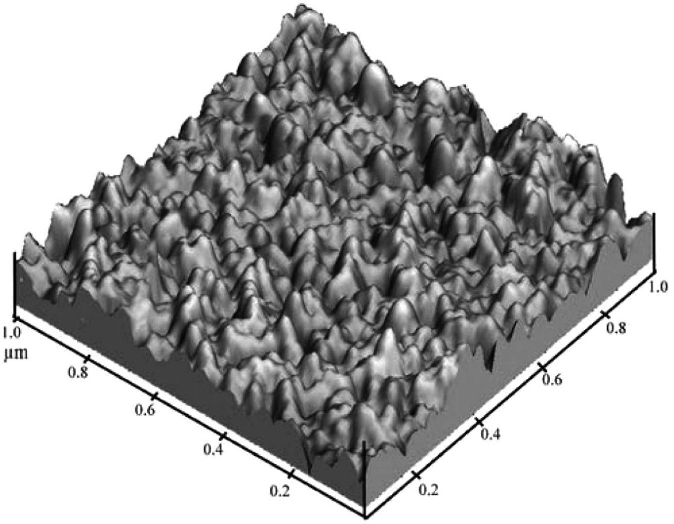

FIGURE 2 AFM image of a PANI film on the surface of an *n*-type (100) silicon single crystal.

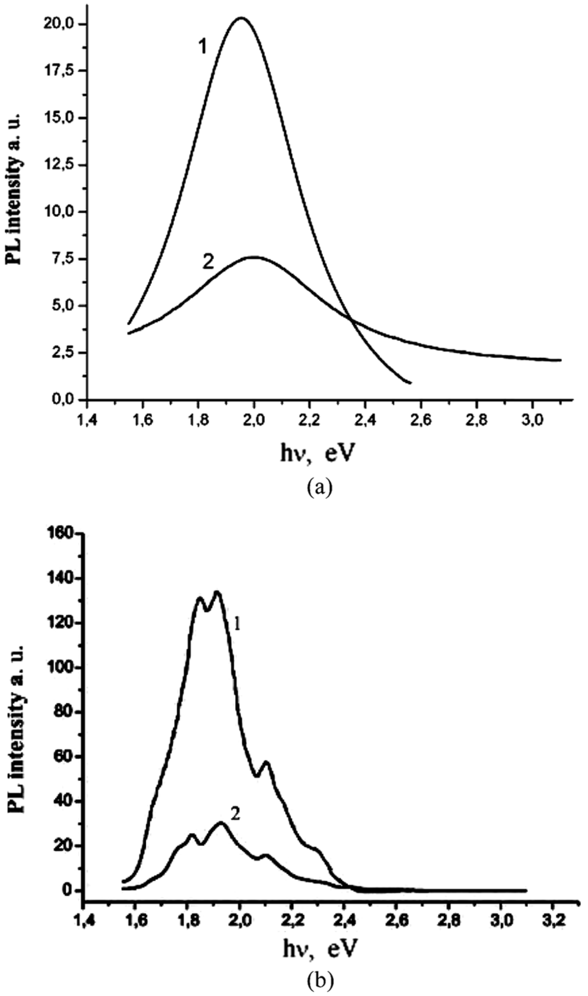

FIGURE 3 (a) Spectra of photoluminescence in the *n*-PS (1) and *n*-PS–PANI (2) heterostructures; (b) in *p*-PS (1) and *p*-PS–POMA (2) heterostructures.

making possible the annihilation of excitons which are spatially limited (trapped) in the intermediate area [11,12]. On the other hand, the emission may be caused by the complexes of Si:O:H, H:Si:H, siloxen $Si_6H_3O_6$ and its modifications [9] formed during the etching process. In complicated complexes of the siloxen type, there is a possibility for clusters to be formed from the silicon atom planes, where the quantum limitation effect also takes place. The PS emission may be considered as a process of monomolecular recombination, which is limited by tunneling across a potential barrier, or as the bimolecular process of recombination of an electron and a hole being free or bound to an exciton [9]. If the recombination proceeds along the radiating channels of nano-crystal grains, the PS being coated by a conducting polymer could significantly affects the recombination mechanism.

It has been found that, after coating the film on the PS surface, the "red" PL is preserved, but its decrease by a factor of 2–3 takes place (for PS−PANI). A weak shift of the PL peak to the short-wavelength region from 1.95 to 2.0 eV may be due to the non-uniform transmittance of the doped PANI film (the transmittance window is close to the emission peak of PS). At the same time, for the PS−PANI heterostructure in the spectra of PL, the weak emission extending to the short-wavelength region, which is probably connected with the intrinsic PL of polyaniline, has been observed [10]. In the case of the PS−POMA heterostructure accompanied by a total decrease of the PL intensity (by 8–10 times) caused by the polymer film absorption, a relative change of the PL band intensity is observed in the interval of 1.9–2.2 eV (Fig. 3b). The obtained results enable us to conclude that a conducting polymer film on the PS surface is not only a passivation layer, but is also capable of interacting with the surface of PS, affecting the PL characteristics.

The most interesting results have been obtained in the study of the CL of PS−CP heterostructures. As has been found, the presence of a polymer layer on the PS surface causes different effects on the cathode emission intensity.

Single crystals of Si are known not to develop any CL (as well as EL) spectra even at very high excitation energies and at low temperatures [8,15]. At the same time, the existence of a nano-porous layer of PS makes the emission possible under the action of a cathode beam. The CL for PS was observed in [16], where a band of CL with a maximum of about 680 nm was manifested. These results are in good agreement with the data of the present paper (Figs. 4 and 5). The spectra with maximum and minimum CL intensities registered from different sections of the non-uniform surface of PS showed that the largest deviation in the PC peak intensity does not exceed 10–15%. Taking into account the great thermal dissipation losses, the efficiency of CL cannot be more than 30–40% [14].

It has been established that CL is observed at the electron excitation of heterostructures based on PS and CP fabricated with the use of various methods (electropolymerization, vacuum deposition, and spin-coating). Furthermore, the spectrum shape and the character of its change in comparison with the CL spectrum of the initial PS

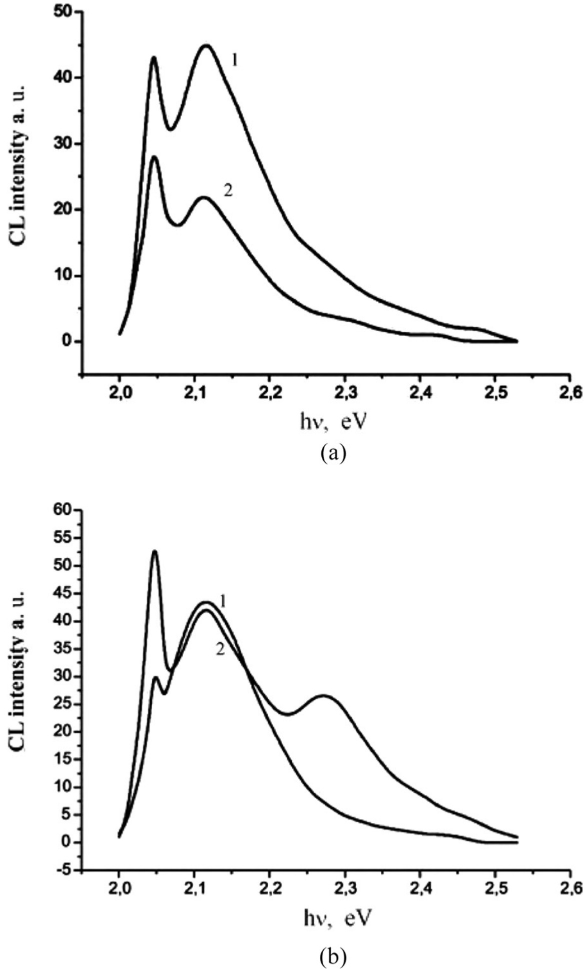

FIGURE 4 (a) Spectra of cathode luminescence in the *p*-PS (1) and *p*-PS−POMA (2) heterostructures; (b) in the *p*-PS (1) and *p*-PS−PANI (2) heterostructures.

(at T = 80 K) depend on the electron and molecular structures of the polymer, as well as on the coated layer thickness.

Similar to PL spectra, conjugated polymers of the aminoarene type (PANI and POMA) affect the CL spectrum in different ways. After the formation of a polymer film on the PS−POMA heterostructure, the spectrum intensity decreases by about 8 times (Fig. 4a), while the peak position in the CL spectrum is not practically changed. In the

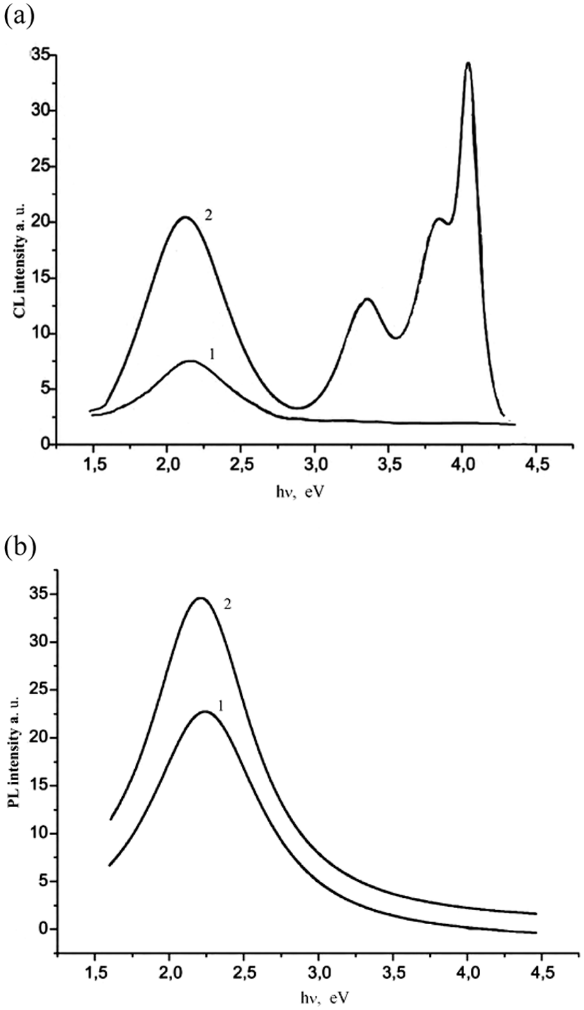

FIGURE 5 (a) Spectra of cathode luminescence in the *p*-PS (1) and p-PS−PPP (2) heterostructures and (b) in the *n*-PS (1) and *n*-PS−PPA (2) heterostructures.

case of PANI, the total intensity of CL increases by about 1.5 times (Fig. 4b), and another broad maximum of emission at 2.27 eV appears. The increase of the CL intensity for the PS−PANI heterostructure is in good agreement with visible electroluminescence obtained for such a configuration [11] due to the electron-hole recombination in nanorods of PS.

So far there are only few data on the luminescence properties of the heterostructures based on other classes of conducting polymers, such as polyarene, polyacetylene, and polycarbazole. At the same time, it is known that such polymers as PPP, PPA, and PEPC exhibit the PL and capability of EL in sandwich-like structures [3,17] mostly developed for PPP [18,19].

It has been found that the intensity of CL for PPP and PPA integrated into PS significantly increases (from 7 to 15 times), while it varies slightly in the case of PEPC. The most remarkable increase of the CL intensity is observed for the PS−PPP heterostructure (Fig. 5). At the PPP layer thickness of 300 ± 20 nm, a rather intense series of CL peaks is observed in the short-wave area of the spectrum at 3.5–4.5 eV, which can be caused by the interband irradiative recombination in the conducting polymer [19].

CONCLUSIONS

Thus, the heterostructures fabricated in the present work, which are based on porous silicon and a conducting polymer, demonstrate a visible luminescence and the capability of the emission under electron beam excitation. The effect of a surface layer on the character of emission processes is defined by the type of a conducting polymer integrated into PS. The obtained results make it possible to assume the presence of the electroluminescence properties in PS-PPP and PS-PPA heterostructures that can be taken as a prototype for multilayered heterostructures in integral optoelectronics.

REFERENCES

[1] Kang, Y., Park, N.-G., & Kim, D. (2005). *Appl. Phys. Lett.*, *86*, 113101.

[2] Stakhira, P. Y., Cherpak, V. V., Vertsimakha, Ya. I., Aksimentyeva, O. I., Dorosh, O. B., & Savchyn, V. P. (2005). *Mol. Cryst. Liq. Cryst.*, *426*, 277.

[3] Friend, R. H. & Greenham, N. C. (1996). In: *Physical properties of Polymer Handbook* (*AIP Series in Polymers and Complex Materials*), Mark, J. E. (Ed.), Amer. Inst. Phys.: Woodbury, New York, Chapter 8, 479.

[4] Baratto, C., Faglia, G., Sberveglieri, G., Gaburro, Z., Pancheri, L., Oton, C., and Pavesi, L. (2002). *Sensors*, *2*, 121.

[5] Aksimentyeva, O. I., Stakhira, P. Y., & Hlushyk, I. P. (2005). *Eastern-European Journal of Enterprise Technologies*, *17*, 127.

[6] Carpi, F. & De Rossi, D. (2006). *Opt. Laser Techn*, *38*, 292.

[7] Moller, S., Perlov, C., Jackson, W., Taussig, C., and Forrest, S. R. (2003). Nature, *426*(6963), 166.

[8] Svechnikov, S. V., Kaganovich, E. B., & Manoilov, E. C. (1998). *Sem. Phys. Quant. Elect. Optoel*, *1*, 13.

[9] Beliakov, L. V., Makarova, T. L., Saharov, V. I., & Serenkov I. T. (1998). *Phys. Tech. Sem.*, *32*, 1122.

[10] Jayachandran, M., Paramasivam, M., Murali, K. R., & Trivedi, D. C. (2001). *Mater. Phys. Mech.*, *4*, 143.

[11] Halliday, D. P., Eggleston, J. M., & Adams P. N. (1997). *Synth. Metals*, *85*, 1245.

[12] Blonskyy, I., Brodyn, M., Vakhnin, A., Kadan, V., and Kadashchuk, A, (2001). *Phys. Lett. A*, *279*, 391.

[13] Stakhira, P., Aksimentyeva, O., Mykytyuk, Z., & Cherpak, V. (2005). *Func. Mat.*, *12*(4), 807.

[14] Pankove, J. I. (1971). *Optical Processes in Semiconductors*, Prentice-Hall: Englewood Cliffs, New Jersey.

[15] Zotti, G., Cattarin, S., & Comisso, N. (1987). *J. Electroanal. Chem.*, *235*, 259.

[16] Yong, Z., Jin Jin Yi., & Yong, N. (1994). *Luminescence*, *60–61*, 404.

[17] Heeger, A. J. (2002). *Synth. Metals*, *123*, 23.

[18] Guha, S., Rice, J. D., Yau, Y. T., Martin, C. M., Chandrasekhar, M., Chandrasekhar, H. R., Guentner, R., Scanduicci de Freitas, P., and Scherf, U. (2003). *Phys. Rev. B*, *67*, 125204.

[19] Lee, C. H., Kang, G. W., Jeon J. W., Song, W. J., and Seoul, C. (2000). *Thin Solid Films*, *363*, 306.