Hybrid nanostructures based on the conducting polymers incorporated to porous silicon matrix

L Monastyrskyi, O Aksimentyeva

1. Introduction

The nanostructures based on inorganic and organic semiconductors including the conducting polymers have attracted a great attention due to the prospect of using such structures in the solar cells, light emitting diodes, sensors, lasers and memory devices [1-5]. Embedding semiconductor nanocrystals in a conjugated polymer matrix has results in significant change in luminescent and photoelectric properties [2]. Belong the semiconductor materials a special place is occupied by the heterogeneous systems based on nanoporous silicon (PS), having a wide application in optoelectronic and sensor devices [6, 7]. 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 [8, 9]. So far there are only few data on the luminescence properties of heterostructures based on other conducting polymers, such as polyphenylacetylene (PPA), polyeoxypropyle carbazole (PEPC), polyparaphenylene (PPP). At the same time, it is known that PPP, PPA, PEPC exhibit the electroluminescence in the sandwich like structures, mostly developed for PPP [10]. In the present work an influence of integrated polymer on the molecular spectra, morphology of surface and luminescence characteristics of PS – conducting polymer (PPP, PPA, PANI, PEPC) nanostructures has been studied.
2. Experimental

The porous silicon layers were obtained by oxidization of the single crystal silicon wafers both n-type (111) and p-type (100) of conductivity with 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 10 mA cm\(^{-2}\) and under illumination by a 150 W tungsten lamp during 10-20 minutes.

For creation of PS-PANI hybrid layer a method of electrochemical polymerization with cyclic potential sweeping in 0.1M solutions of purified aniline in 0.5 M H\(_2\)SO\(_4\) was used. A wafer of PS of the area of 1 cm\(^2\) was as an operating electrode, a platinum wire was used as a counter electrode and saturated Ag/AgCl electrode was employed as a reference. The potentiostat PI-50 was a power source. After coating the film as described in [11] the samples were rinsed with deionized water and dried under vacuum at 353 – 373 K.

Magnetron deposition of the conducting polymers on the porous silicon surface was carried out on the URM-3 equipment in the argon atmosphere at residual pressure 5x10\(^{-3}\) mm Hg on the frequency of 13,56 MHz in the magnetic field 0,1 Т at the power of 100 W. The middle rate of condensation was \(\approx\) 2 nm/min. Formation of PS-PPA and PS-PEPC heterostructure was carried out by dip coating method from polymer solution in chloroform.

The molecular structure of the obtained hybrid layers were studied by FT-IR spectroscopy with AVATAR 320N spectrophotometer in the spectral region of 4000 – 400 cm\(^{-1}\). The morphology of the hybrid layer was studied by scanning electron microscope JEOL JSM – T220A and by atom force microscopy (AFM) with SZM SOLVER PRO-M microscope.

Photoluminescence (PL) was excited by pulse nitrogen laser LGI-21 (337.1 nm), pulse duration \(\tau_p\) = 20 ns, at frequency of 60 Hz. The measurements were carried out both at room temperature and of temperature of the liquid nitrogen. Cathode luminescence was excited by pulse electron flow with energy \(E_p\)=9 keV, with 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.

3. Results and Discussion

To study the character of the surface topology of the obtained heterostructures the two methods – scanning electron microscopy (SEM) and atom-force microscopy (AFM) has been employed. The surface of PS has a shape of vertical nanorods created due to the etching of separate places of a single silicon surface (Fig.1,a). As a result of profile analysis of AFM-images it is defined that the pore depth achieves 180 - 200 nm at total thickness of porous layer about 5 µm.

The PANI films obtained on the surface of PS by electropolymerization method also as dip-coated PPA film in general repeat the relief of the surface forming a continuous polymer layer (Fig.1, b). However, the morphology of the films is difficult interpret due to the irregularity of PS surface. As has been shown by the profile analysis of PS-polymer heterostructure a thickness of PS-polymer layer achieves 40–45 nm. In the process of magnetron deposition the polymer is formed as permanent nanofilm on the porous silicon surface (Figure 2, a) and also may deposit inside silicon pores which is clearly demonstrated for PS-PPP heterostructure (Figure 2, b).
Figure 1. AFM images of the porous silicon surface (a) and porous silicon – polyaniline hybrid structure (b)

FIGURE 2. SEM microphotos of the porous silicon - conducting polymer nanostructures obtained by magnetron deposition: a) PS-PANI (x 1000); b) PS-PPP (x 5000)

The photoluminescence spectra of porous silicon studied in the spectral range of 1.5-3.1 eV are in good agreement with the ones described in literature [6-9]. It has been found that in hybrid PS-polymer nanostructures the “orange - red” photoemission is preserved, but it decreasing by a factor of 2 – 3 takes a place (Figure 3). A weak shift of PL peak may be due to non-uniform transmittance of the conducting polymers (the transmittance window is close to the emission peak of PS).

An appearance of luminescence of the porous silicon in the visible range of spectrum may be explained by some ideas. From the one hand the quantum size effects making possible the annihilation of the excitons which are spatially limited (trapped) in the intermediate area [6]. On the other hand emission may be caused by the complexes of Si:O:H, H:Si:H, siloxen Si₆H₉O₆ and its modifications [7] formed during the etching process. PS emission may be considered as a process of monomolecular recombination, limited by tunneling across the potential barrier, or as bimolecular process of recombination of the electron and the hole being free or bound to the exciton [12]. At the same time, it is known that such polymers as PPP, PPA and PEPC may be active layer in the electroluminescence devices [10].
FIGURE 3. Photoluminescence spectra of PS (1); PS-PANI (2); PS-PPP hybrid structure at 293 K.

As a test on the ability to electroluminescence may be study of cathode luminescence exited by electron beam [13] without special metal contacts.

It known that in silicon single crystal any CL (as well as EL) does not develop even at very high excitation energies and at low temperatures. At the same time, the existence of PS nanostructured layer makes it possible to excite the light emission under the action of the cathode beam. We observed the cathode luminescence of the porous silicon with a band maximum near 2.12 eV which is in good agreement with the data described in [14].

The cathode luminescence is observed at electron excitation of heterostructures based on PS and conducting polymers, fabricated by different methods (electropolymerization, magnetron deposition and dip-coating). Furthermore, the shape of the spectrum and the character of its change in comparison with CL spectrum of initial PS (at T = 80 K) depends on the electron and molecular structure of polymer.

FIGURE 4. CL spectra of (a) PS (1), PS-PEPC (2); (b) PS (1) and PS-PPP (2) hybrid structure

It is found that PANI and PEPC polymers integrated with PS cause a slow increasing in CL intensity (Figure 4, a). At the same time an intensity of CL significantly increases at the presence of PPP and PPA in hybrid layers as compared with CL in porous silicon matrix without polymer (Figure 4, b).
According to the FT-IR spectroscopy (typical spectra presented in Figure 5) the surface of PS, obtained by electrochemical etching the silicon wafer in HF alcohol solution, contains the different functional groups with characteristic absorption bands at 2900-3620 cm\(^{-1}\) (\(-\text{OH}\)), 1100 cm\(^{-1}\), 1240 cm\(^{-1}\) (Si-O-Si), 1111 cm\(^{-1}\) (C-O), 1072 cm\(^{-1}\) (CH-OH), 620 cm\(^{-1}\) (Si-H\(_2\)) and others (Fig.5,a).

**FIGURE 5.** FT-IR spectra (a) of porous silicon (insert – PPA on KBr) and (b) of PS-PPA hybrid structure

In result of polymer adsorption an activation of several bonds (for example -N-H for polyaniline or -C=C-H- for PPA) and creation the new passivative complexes with surface silicon bonds may proceed. The evidences to such interaction are the shifts of the Si-O-Si absorption band from 1100 and 1240 cm\(^{-1}\) to 1050 and 1250 cm\(^{-1}\), also as appearance of the new bands, do not observed in porous silicon and polymer spectrum (Fig.5,a, insert), with maximums at 1188 (C-C), 1280 (Ar-0H) and 1770 (C=O) cm\(^{-1}\) (Fig. 5, b). These bands may be assigned to formation of the weak covalent bonds between polymer and semiconductor due to polymer chemosorption on the active centres (Si-O-Si) of the porous silicon surface, probably with formation of light emissive complexes [7]. It is assumed that a rate of non-radiation surface recombination decreases at coating the PS surface with polymer due to the passivative action of the polymer. Apparently, this causes the increase in the radiation component of recombination as well as the increase in CL intensity. If recombination proceeds along the radiating channels of the nanocrystal grains, the PS being coating by a conducting polymer could significantly effects the recombination mechanism. From the other hand increasing in CL intensity may be caused by the interband radiation recombination in the conducting polymer [10, 15] deposited in nanopores of silicon.

5. Conclusion

The fabricated hybrid semiconductor – polymer nanostructures based on porous silicon and conducting polymer demonstrate a visible luminescence and the capability to light emission under electron beam excitation. The effect of the hybrid structure on the character of emission processes is defined by the type of conducting polymer integrated into PS. According to FT-IR spectroscopy the some interaction between polymer functional groups and porous silicon surface takes a place. We have assumed, it is leading to decreasing a rate of non-radiating surface recombination and to increasing the radiation component of recombination as well as increasing in the CL total intensity. An increasing the luminescence intensity may be also caused by the interband radiation recombination in the conducting polymer deposited in confinement of the silicon nanopores.
An “anomalous” increasing in quantum efficiency of the cathode luminescence at absorption of polymers by the porous silicon surface can be interpreted by the effects which are inverse those leading to decrease of the emission. In particular, during the process of polymer deposition it is possible an activation of certain polymer bonds and creation the new passivative complexes with dangling silicon bonds. It is clear that such aggregation of silicon atoms gives rise to increasing the quantum efficiency of emission that is observed experimentally. The degree of influence of the polymer’s cover has depends on the character of pores filling by polymer and the magnitude of dipole moment of the adsorbed polymer in the hybrid structures. At larger dipole moment there is occurs trapping of an electron or hole on the energy levels, i.e. the rate of Shockley-Read non-radiation recombination via these levels increases.

5. References

[1]. Kang,Y., Park, N.-G., Kim, D. 2005 Appl. Phys. Lett. 86 113101
[2]. Bakueva L., Musikhin S., Sargent E.H. Shik A. 2003 Surface Science 532-535 1051
[3]. Aksimentyeva O.I., Poliovyi D.O., Fechan A.V., Yevchuk O.M. 2008 MCLC 497 362
[4]. Baratto, C., Faglia, G., Sberveglieri, G., et al. 2002 Sensors 2 121
[5]. Aksimentyeva O., Monastyryski L., Savchyn V., Stakhira P.Y. 2007 MCLC 467 73
[6]. Svechnikov S.V., Kaganovich E.B., Manoilov E.C. 1998 Sem.Phys.Quant.Elect.Optoel. 1 13
[7]. Beliakov L.V., Makarova T.L., Saharov V.I., Serenkov I.T. 1998 Phys.Tech. Sem. 32 1122
[8]. Jayachandran M., Paramasivam M., Murali K.R., Trivedi D.C. 2001 Mater.Phys.Mech. 4 143
[9]. Halliday, D.P., Eggleston, J.M., Adams, P.N. 1997 Synth.Metals 85 1245
[10]. Lee C.H., Kang G.W., Jeon J.W., et al. 2000 Thin Sol. Films 363 306
[11]. Stakhira, P., Aksimentyeva, O., Cherpak, V. 2005 Phys.Chem.Sol.State 6 (2) 235
[12]. Blonskyy, I., Brodyn, M., Vakhnin, A., et al. 2001 Phys.Lett.A. 279 391
[13]. Pankove J.I. 1971 Optical processes in semiconductors (Englewood Cliffs: New Jersey, USA)
[14]. Yong, Z., Jin Yi, Jin, Yong, N., 1994 Luminescence 60-61 404
[15]. Heeger, A.J. 2002 Synth.Metals 123 23