Electrosynthesis of Intrinsically Conducting Polymers/Silicon Nanocomposites: Formation Mechanism and Optical Properties

F. A. Harraz[*] and A. M. Salem

Nanostructured Materials and Nanotechnology Division, Central Metallurgical Research and Development Institute (CMRDI), P. O. Box: Helwan, Cairo 11421 Egypt, fharraz@cmrdi.sci.eg

ABSTRACT

Nanocomposites of various conducting polymers and porous silicon have been successfully fabricated by the electrochemical and spin coating techniques. Porous silicon template was firstly synthesized by the galvanostatic anodization of silicon wafer in HF-based solution, followed by the electrochemical polymerization of polypyrrole (PPy), polyaniline (PAn) and polythiophene (PTh). The results of the electropolymerization reveal that the polymers are infiltrated homogeneously inside the nanopores. The deposition starts from the pore bottom and propagates towards the pore opening. The deposition of Poly(2-methoxy-5-(2-ethyl-hexyloxy)-1,4-phenylene-vinylene) MEH-PPV was also performed into the porous silicon matrix using the spin coating technique. As-formed nanocomposites have been fully characterized using various techniques including, SEM, XRD, FTIR. The photoluminescence behavior was examined and evaluated.

Keywords: porous silicon, conducting polymers, electrochemical technique, optical properties

1 INTRODUCTION

Intrinsically conducting polymers are polymers with a highly π-conjugated polymeric chain [1]. For the past several decades, polymers have increasingly been used as insulators in the electronic devices and integrated circuits. In the year 1975, polythiazyl was discovered as the first conjugated polymer that possesses metallic conductivity. However, the idea of using the electrical conducting properties of polymers emerged in 1977 with the amazing finding of Shirakawa et al [2], that a "thin film of polyacetylene could be oxidized with iodine vapor, increasing its electrical conductivity a billion times". This actually opened a new field of processing and development of conducting polymers. As a result, in the year 2000 the Nobel Prize in Chemistry was awarded to Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa for their novel work in the field of conductive polymers. The improved electrical conductivity is not only the unique property for such polymers but also the promising physicochemical properties in general and good stability that can be achieved from these materials. Depending on the method of preparation, chemical modification and the way and nature of doping process, the electrical properties of these polymers can be tuned from insulating, semiconducting and metallic regime. Such polymers are usually synthesized from the appropriate monomers by either chemical or electrochemical oxidative polymerization technique. Electrochemical polymerization is conveniently carried out at metallic substrates or carbon electrode materials, whereas no polymeric films can be obtained on insulating surfaces.

From the technological point of view, conducting polymers have the ability to be explored in various applications, including light emitting diodes [3], wave-guides [4], sensors [5], corrosion protections [6], and photovoltaic devices [7]. The key point for fulfilling high performance of such devices using conjugated polymers is to fabricate a highly organized structure on a surface on a single-molecular scale [8]. In our previous works we have deposited PPy into porous silicon templates [9-13]. In this contribution, chemical and electrochemical synthesis of a group of conducting polymers, mainly PPy, PAn, PTh and MEH-PPV into porous silicon templates are presented with a focus to understand the polymerization process and evaluate the morphological and optical properties of as-formed nanocomposites.

2 EXPERIMENTAL

Porous silicon templates were fabricated in n-type Si(100) substrate, resistivity 0.010-0.018 Ωcm by galvanostatic anodization in 6 wt.% HF + 8 mM $KMnO_4$ + 1000 ppm ethanol at 10 mA/cm^2 for 5 min. Before the porous silicon formation, the silicon wafer was pre-treated in acetone with ultrasonic for 10 min, followed by rinsing in 5 wt.% aqueous HF to remove the native oxide. The average pore size of as-synthesized porous silicon was less than 50 nm. The electrochemical polymerization was conducted in 0.01 M of the corresponding monomers (Py, An and Th) in acetonitrile solution in the presence of 0.1 M tetra-butyl-ammonium perchlorate as a supporting electrolyte at 200 µA. MEH-PPV was deposited from 0.025 g MEH-PPV dissolved in 100 ml chloroform at 2000 rpm for 1 min and the spin coating was repeated on the wet substrate for 10 times. Then the porous silicon containing MEH-PPV was dried at 100 °C for 1 h. The chemical structures of the four polymers are depicted in Fig.1. The as-formed nanocomposites were imaged by SEM. XRD and FTIR were also measured. Photoluminescence for porous silicon with no polymer and the conducting polymer/porous silicon nanocomposites were measured by means of

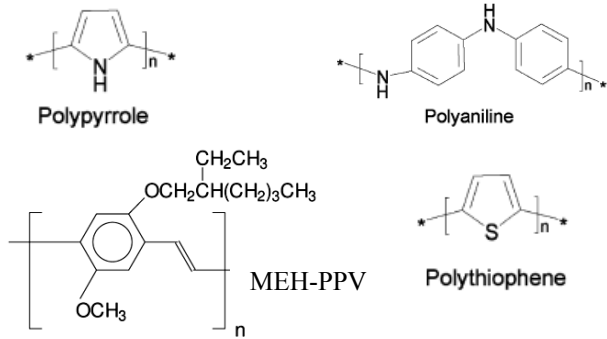Spectrofluorophotometer, SHIMATDZU RF-5301PC using a 150 W xenon lamp as an excitation source.

Figure 1: Chemical structures of studied conducting polymers

3   RESULTS AND DISCUSSION

Figure 2 shows a typical potential transient recorded during the polymerization of PTh into porous silicon template at a constant current 200 µA. At the early stage of polymerization, the potential rises during the polymer nucleation at the pore bottom. The potential was then nearly leveled at around 1.6 V during the polymer growth stage. Once the pores are completely filled with PTh, indicated by an arrow in Fig.2, a sharp potential rise is observed which is corresponding to the change of deposition site from inside the pores to outside the surface. Such potential rise is related to the deposition of bulk polymer onto the outer surface of porous silicon. The amount of polymer deposited in the interior of the nanopores can be controlled by the value of the polymer-formation charge within the period before such transition stage. Similar deposition behavior was observed for both PPy and PAn under the identical deposition conditions.
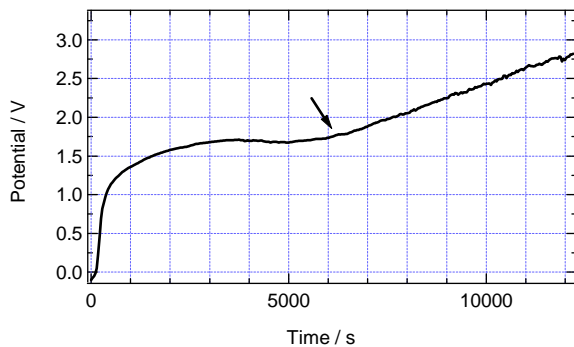

Figure 2: Potential transient recorded during the galvanostatic polymerization of thiophene into porous silicon matrix at 200 µA.

The electrodeposited conducting polymers into porous silicon matrices were inspected using SEM. Top and cleaved cross-sectional views were recorded for the three different polymers (PPy, PAn, PTh) in addition to the cross-

sectional view of the spin coated MEH-PPV into porous silicon (Fig.3). The bright areas inside the porous silicon layers are corresponding to polymer deposition. The uppermost part in all images shows a thin film of polymer deposited outside the surface. The bulk conducting polymers grown at the outer template surface is shown in the top-view images of Fig.3 (a-2, b-2 and c-2). In case of MEH-PPV (image d-1), one can easily observe the polymer deposition at the top opining pores as well as scattered bright parts inside the nanopores. Here one may conclude that using the electrochemical or the spin coating technique, the conducting polymers could be infiltrated efficiently into the nanopores created in silicon substrates.
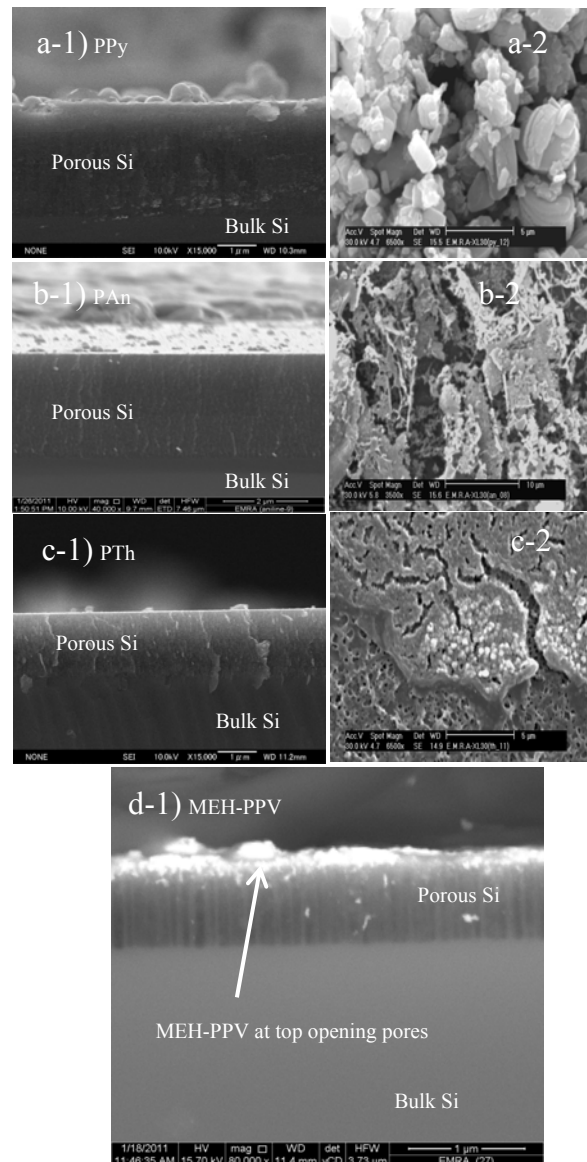

Figure 3: SEM images of cross-sectional view (a-1, b-1, c-1 and d-1) and top views (a-2, b-2 and c-2) of porous silicon deposited with different polymers.

X-ray diffraction patterns were measured for as-fabricated polymeric nanostructures. The XRD pattern shown in Fig.4 revealed that the resulting polymer structures are amorphous showing a broad band in the region of $15° < 2\Theta < 28°$, indicating that short-range chain arrangement of polymers is dominating in this study. The XRD results are in agreement with previous reports on PPy nanowires fabricated by electrochemical [14] and chemical polymerization [15].
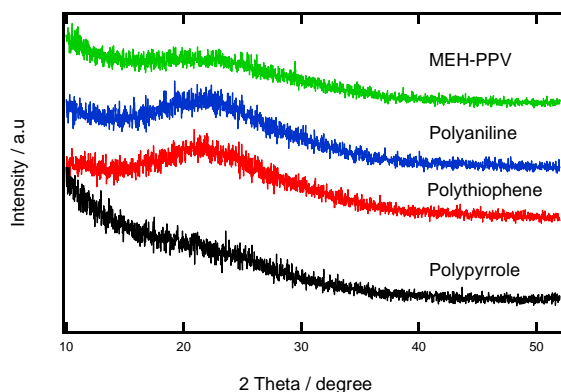

Figure 4: X-ray diffraction patterns of as-formed PPy, Pan, PTh and MEH-PPV into porous silicon

FTIR was measured for the deposited polymeric films. An example is given in Fig. 5 for the case of MEH-PPV after spin coating into porous silicon. The characteristic peaks of the MEH-PPV conducting polymer as well as the complete assignments of the bands are listed in Table 1. The characteristic band of (RO)-CH$_2$ asymmetric vibration is observed at 1445 cm^{-1} for polymer film. Furthermore, the as-deposited MEH-PPV film reveals a band at 1736 cm^{-1} due to formation of aromatic aldehyde (C-O stretch) [16].
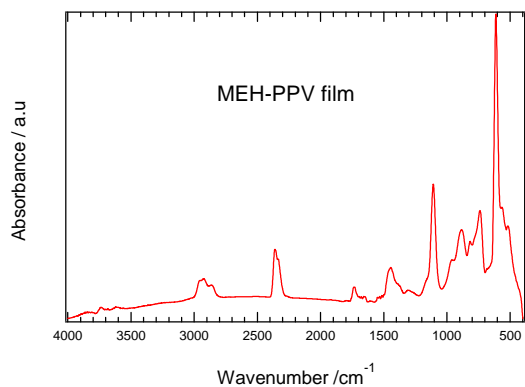

Figure 5: FTIR spectra recorded for MEH-PPV film spin coated into porous silicon.

The optical properties of as-formed hybrid structures were evaluated by measuring the photoluminescence (PL) spectra. The PL was firstly measured for as-formed porous silicon and porous silicon filled with conducting PPy, PAn and PTh polymers. Figure 6 shows the PL spectra of porous silicon (with no polymer deposition) and PPy, PAn and PTh electrodeposited into porous silicon.

Peak position (cm^{-1})	Peak assignments
2955	CH$_3$ asymmetric stretching
2924	CH– stretching
2863	CH$_2$ stretching
1736	Formation of aromatic aldehyde
1606	Aromatic stretching
1445	Antisymmetric phenyl stretch
1108	Si-O-Si stretching
965	*Trans*-double bond CH-wag (vinyl group)
882	Out of plane phenyl CH-wag
736	Out of plane ring bend of phenyl ring

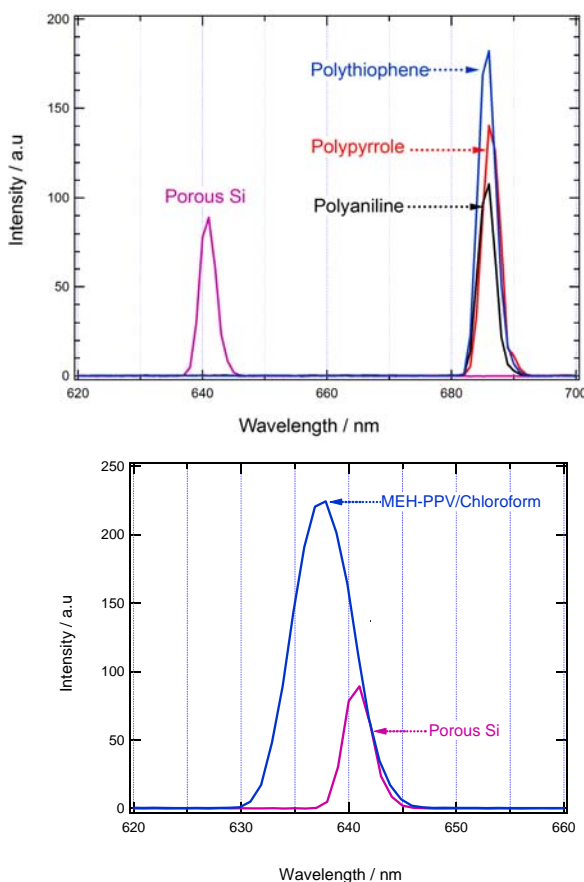Table 1: FTIR peak assignments for MEH-PPV deposited into porous silicon by spin coating.

Figure 6: Room temperature photoluminescence spectra of as-formed porous silicon (without polymer) and conducting PPy, PAn, PTh polymers-electrodeposited porous silicon (top Fig.) and MEH-PPV spin coated porous silicon (bottom Fig.)

All the samples were exited at 320 nm excitation wavelength. As can be seen, the unmodified porous silicon layer exhibits PL peak at 641 nm (1.93 eV). After the electrochemical deposition of conducting PPy, PAn and PTh polymers into porous silicon matrices, the PL intensity was significantly enhanced and the peak was red-shifted to 686 nm (1.81 eV), compared to the porous silicon PL peak. This corresponds to a shift of 120 meV towards the longer wavelength. The highest increase of peak intensity was found for the case of PTh electrodeposited into porous silicon; the intensity of the PTh peak was 2 times higher than that of the one without PTh-deposited porous silicon. The PL enhancement was in the order PTh > PPy > PAn.

We measured also the fluorescence PL spectra of MEH-PPV polymer film prepared by spin coating in polymer-chloroform solution into porous silicon template. Ten continuous layers of polymer were deposited at 2000 rpm, 1 min for each layer, followed by drying the nanocomposite at 100°C for 1 h. An important finding of Fig. 6 (bottom) is noted as the PL peak intensity of the nanostructure after polymer coating is highly enhanced and slightly blue-shifted compared to the emission peak observed for porous silicon

Based on the above PL results, the increase in PL intensity with conducting polymers deposition may be attributed to the passivation of surface states in porous silicon in a way to reduce the dangling bonds. Under this condition, the closely spaced surface states of porous silicon can act as continuous energy levels and thus transfer the energy to the conduction band of conducting polymers giving off the emission. In addition, due to the presence of pores, the PPy, PAn, PTh and MEH-PPV molecules are separated by the pore walls, which in turn decrease the collision of polymer and increase the conjugation of molecules, which could enhance the emission of conducting polymers.

4   CONCLUSIONS

A group of conducting polymers has been successfully deposited into porous silicon templates with pore sizes in the range of 50 nm. The electrochemical technique was applied to deposit PPy, PAn and PTh into porous silicon templates, whereas the MEH-PPV polymer was infiltrated into porous silicon via spin coating method. The as-formed nanocomposites have been characterized using different techniques, including SEM, XRD, FT-IR and photoluminescence spectra measurements. The results revealed that, the fluorescent light intensity of the composites of porous silicon with conducting polymers was significantly enhanced while the emission peak position was red-shifted in case of PPy, PAn, and PTh and blue-shifted in case of MEH-PPV. It is assumed that the exciton transfer may take place from the porous silicon matrix to the conducting polymers which needs further study for better understanding and clarification.

REFERENCES

[1]   X. Lu, W. Zhang, C. Wang, T.-C. Wen and Y.Wei, Progress in Polymer Science, 36, 671, 2011

[2]   H. Shirakawa, E. J. Louis, A. G. MacDiarmid, C. K. Chiang and A. J. Heeger, J. Chem. Soc. Chem. Commun. 578, 1977.

[3]   V. Saxena ans B. D. Malhotra, Current Appl. Phys. 3, 293, 2003.

[4]   R. M. L. Van de Leur and A. Van der Waal, Synth. Met. 102, 1330, 1999.

[5]   J. C. Vidal, E. Garcia and J. R. Castillo, Anal. Chim. Acta, 381 (1−3), 213, 1999.

[6]   G. S. Akundy and J. O. Iroh, Polymer, 42, 9665 2001.

[7]   K. Tada and M. Onoda, Thin Solid Films, 477, 187, 2005.

[8]   C. D. Dimitrakopoulos and D. J. Mascaro, IBM J. Res. Dev. 45, 11, 2001.

[9]   F. A. Harraz, S. M. El-Sheikh, T. Sakka and Y. H. Ogata, Electrochim. Acta, 53, 6444, 2008.

[10] F. A. Harraz, J. Electrochem. Soc. 153 (5), C349, 2006.

[11] F. A. Harraz, M. S. Salim, T. Sakka and Y. H. Ogata, Electrochim. Acta, 53, 3734, 2008.

[12] K. Fukami, F. A. Harraz, T. Yamauchi, T. Sakka and Y. H. Ogata, Electrochem. Commu. 10, 56, 2008.

[13] F. A. Harraz, Physica Status Solidi (C) 8 (6), 1883, 2011.

[14] H. Yan, L. Zhang, J. Shen, Z. Chen, G. Shi and B. Zhang, Nanotechnology, 17, 3446, 2006.

[15] S. C. Hernandez, D. Chaudhuri, W. Chen, N. V. Myung and A. Mulchandani, Electroanalysis, 19, 2125, 2007.

[16] M. Ram, N. Sarkar, P. Bertoncello, A. Sarkar, R. Narizzano and C. Nicolini, Synthetic Metals, 122, 369, 2001.