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Study of optical and electrical properties of thin films of the conducting comb-like graft copolymer of polymethylsiloxane with poly(3-hexyltiophene) and poly(ethylene) glycol side chains for low temperature NO_2 sensing

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ABSTRACT

This work presents an investigation on graft comb copolymer of polymethylsiloxane (PMS) with poly(3-hexyltiophene) (P3HT) and poly(ethylene) glycol as functional side groups. This segmented copolymer was investigated as a NO_2 gas sensing material. Gas sensing, optical and electrical properties of thin films of graft polymers and clean P3HTs (regioregular and regiorandom) are tested and compared. The thin films of investigated materials obtained by spin coating method on interdigital transducers and surface plasmon resonance (SPR) sensor structure are characterized by using atomic force microscopy method and Raman spectroscopy. High changes of resistance and SPR signal caused by action of NO_2 in the concentration of ppm range were observed. It showed that such graft polymers are promising materials for resistance and optical gas sensors operating at low temperatures. Obtained results showed that resistance and sensitivity of graft polymers depend on the content of P3HT and PMS backbone chain length. An optical SPR NO_2 gas sensor and resistance NO_2 sensor based on graft polymer thin films display a very fast response time and a fast regeneration time at low temperature (50 °C) in a dry gaseous environment. Resistance sensor investigation showed that the sensitivity of graft polymers to 5 ppm of NO_2 can be about 20 times higher than in the case of clean P3HTs.

1. Introduction

Conducting polymers such as polythiophene (PT), polyaniline and polypyrrole are nowadays used in the areas of optoelectronic devices, solar cells, field-effect transistors and chemical sensors [1–8]. PT is rather inconvenient material due to its poor processability (it is insoluble in conventional organic solvents and it is infusible). Similar properties to PT have poly(alkylthiophene)s (PAT) such as poly(3-hexylthiophene) (P3HT). In addition, PATs are soluble in conventional solvents, for example in chloroform ($CHCl_3$) and toluene. Thus, they are well processable and can be easily applied to the substrates, which results in their popularity in many applications [9–11].

Sensor structures which allow to detect and measure small concentrations of nitric oxides are very important due to their potential applications, for example in medicine, automotive industry, environmental monitoring and detection of explosives [12–15]. Sensors based on semiconductor oxides are generally inexpensive and show high stability [16]. At present, market offers sensors which allow to measure and detect NO_2 at ppm levels at relatively high temperatures [17]. It is related with using semiconductor oxides as receptors because their chemisorption takes place at relatively high temperatures (hundreds of Celsius degree). Decreasing of operation temperature of gas sensors is important in the context of their power consumption. Therefore, it is necessary to develop and fabricate practical, small, and low-cost sensor devices that can detect low NO_2 concentrations at low temperature. This leads to a search for materials showing significant improvement of sensitivity, speed and accuracy of measurement, and consequently, safety. Gas sensors based on organic receptors such as phthalocyanines or conducting polymer layers (including P3HT) become increasingly popular [2,15,18–23]. Our previous works showed that P3HT and its grafts are sensitive to low concentrations of NO_2 [24–26].

The key objective of this study is to achieve highly sensitive and stable chemoresistive and optical sensors with low power consumption by the development of multifunctional, π-conjugated materials, designed to answer the demands of the gas sensor market. In the view of high application potential of gas sensor devices, we postulate the synthesis of graft copolymers of siloxane and π-conjugated macromolecules. These

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materials, featuring varied electron affinities, can be tailored on both a molecular and a supramolecular levels, to exhibit a range of physico-chemical properties.

In organic optoelectronic devices Indium tin oxide (ITO)/glass or ITO/quartz electrodes are typically used. Gas sensors are also often make use of Si/SiO_2 or glass substrates with metal electrodes. Out of many systems interacting with such oxide-based substrates, siloxanes are a prime candidate due to their high affinity for such materials and cost-efficiency. Therefore, grafting conjugated polymers onto siloxane or polysiloxane scaffolds may be sufficient to achieve such an effect [4]. Furthermore, organosilanes can be used to self-organize into layered lamellar structures, whose structure may be controlled to a significant extent [27].

The highly soluble and processable polymer sensor material can be obtained by grafting the synthetic polymers and also by the process of derivatization of grafted polymers to impart a wide array of functional groups causing a stronger specific interaction with the host polymer backbone. Grafting methods enable the synthesis of a wide range of copolymers with controlled molecular weight, narrow molecular weight distribution, and the range of architectures and functionalities [28]. Therefore, the functionalization of a main polymer chain with well-defined functional polymers allows the fabrication of high performance conducting composite sensor materials as segmented copolymers [23,28].

In our work, we have opted to mount one type of conjugated chains – P3HT – and one type of non-conjugated chains – poly(ethylene) glycol (PEG) – onto our host polymer scaffolds. In our case, grafting involves the reaction of functional groups (P3HT and PEG) located at chain ends of one kind of polymer with another functional groups which distributed randomly on the main chain of the poly(methyl-hydro-siloxane) (PMHS) polymer backbone. The choice of P3HT was based on the fact that it is a well-known, hole-transporting system, which could be readily grafted onto a polysiloxane chain in a controlled manner. PEG was used primarily as a molecular disperser, for enhanced control over the average number of P3HT chains attached to a polysiloxane chain. Several basic parameters were varied to produce our systems, which allowed us to observe the complex interplay between the electric and spectroelectrochemical properties of these copolymers and their structure, constituting, what we earnestly believe to be a proof of the laid out concept.

In this paper, gas sensing, electrical and optical properties of obtained polymer are studied. For optical parameters and optical gas sensing properties investigations the wavelength modulated surface plasmon resonance (SPR) was used. The SPR gas sensor is a powerful tool for chemical analysis which provides a rapid, label-free and high sensitive detection of specific gases [21,29–31]. SPR technique allows to detect binding specificity of gas molecules to receptor structures [30]. The SPR sensing principle was based on fixing the angle of the incident light and modulating the wavelength of the reflected light. Standard Kretschmann configuration [21,29–31] was applied to perform the resonant condition by attenuated total reflection (ATR) in a prism. For comparison, the SPR sensor based on rrP3HT, and the SPR sensor based on comb polymer grafted P3HT sensing film were also studied for the detection NO_2.

2. Experimental

2.1. Materials

The commercial regioregular (rr) with head-to-tail head-to-tail ordering ≥90% and regiorandom (nr) poly(3-hexyltiophene-2,5-dyil) (both from Sigma Aldrich) were used. Investigated graft comb polymers were obtained by the method described in the patent application [32]. Synthesis was based on grafting of the P3HT and PEG to poly(methyl-hydro-siloxane) (PMHS) chains (all materials from Sigma Aldrich). The macro particle scheme of the obtained polymethylsiloxane-*graft*-poly(3-hexyltiophene)-*graft*-PEG (graft polymer) is presented in the Fig. 1.

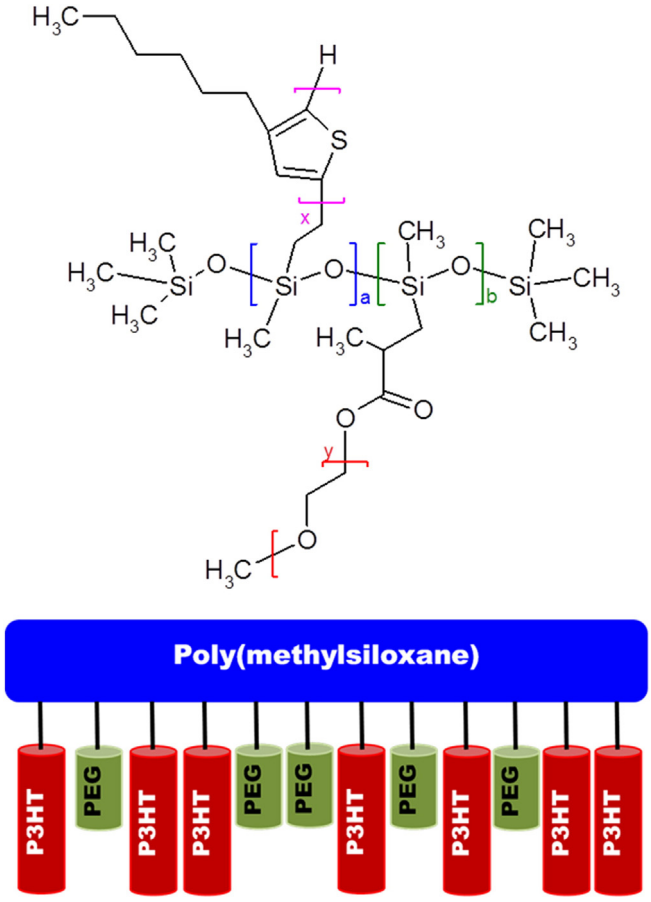

Fig. 1. The chemical structure and block scheme of the Graft macroparticle.

The graft polymers with different polymethylsiloxane (PMS) chain length and P3HT to PEG side groups ratio were obtained. In our investigations two different grafts were taken (Graft 1 and Graft 2). Average PMS molecular weights (M_n) were different in both Grafts, and it were $M_n \approx 390$ and $M_n = 1700–2300$ for Graft 1 and Graft 2, respectively. The weight percent fractions (wt%) of both grafts are collected in the Table 1.

2.2. Preparation of the sensing structures

The way of simple and low cost method of deposition of grafted polymers onto the plasmonic structures and interdigital transducers (IDT) from solutions was investigated in our work. Technology based on spin coating deposition technique was chosen. This inexpensive manufacturing process is suitable for future gas sensor products based on relatively low cost substrates such as Si/SiO_2 with Au electrodes (electronic sensors) and glass slides covered by plasmon active films (SPR sensors).

All used polymers are soluble in $CHCl_3$, therefore in order to apply materials on transducers the solutions of 2.5 mg of every polymer in 1 ml of $CHCl_3$ (stirred with ultrasonic power for 10 min at room temperature) were prepared. The spin coating method with 500 rpm was used where solutions were dropped (single drop of 25 μl) on the rotating

Table 1
The weight percent fractions of Graft 1 and Graft 2 components.

Component	Graft 1	Graft 2
P3HT	12%	9%
PEG	85%	81%
PMS	3%	10%

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