Talanta 153 (2016) 145–151

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Growth and toxic gas sensing properties of poly(urethaneimide) thin films

Ismail Ben Youssef [a,b], Frederic Sarry [a], Bernard Nysten [c], Gergana Alexieva [d], Vesselin Strashilov [d], Iliyan Kolev [e], Halima Alem [a,*]

[a] Institut Jean Lamour (IJL), UMR CNRS 7198, Université de Lorraine, Parc de Saurupt CS50840, 54011 Nancy, France
[b] Laboratoire de Chimie Physique Macromoléculaire (LCPM), UMR CNRS-INPL 7568, Nancy Université, ENSIC, 1 rue Grandville, BP 20451, 54 001 Nancy Cedex, France
[c] Université catholique de Louvain, Institute of Condensed Matter and Nanosciences, Bio & Soft Matter, Croix du Sud 1/L7.04.02, 1348 Louvain-la-Neuve, Belgium
[d] Sofia University, Department of Solid State Physics and Microelectronics, 5 J. Bourchier blvd, 1164 Sofia, Bulgaria
[e] Medical University Varna, Department of Pharmaceutical Sciences and Pharmaceutical Management, 9002 Varna, Bulgaria

ARTICLE INFO

Article history:
Received 20 December 2015
Received in revised form
1 March 2016
Accepted 5 March 2016
Available online 7 March 2016

Keywords:
Functional polyurethanes
Nano-structuration
Sensitive layer
Gas micro-sensor

ABSTRACT

In this work we present a study on the growth and the gas sensing properties of poly(urethane imide) thin films. We first deeply characterized by atomic force microscopy (AFM) the nanostructuration of the poly(urethane imide) holding different amine groups. We further studied the interaction between highly toxic gases such as hexamethyleneimine (HMI) and pyridine and the polymer by using an unconventional method based on Quartz Crystal Microbalance (QCM) measurement. We showed for the first time that weak interactions, i.e. hydrogen bonding between the gas molecules and the polymer film allow the diffusion of the gas molecule deep in the polymeric film and the recovery of the film once the gas molecules leave the sensor. This first work paves a new way for the design of a completely recoverable sensor able to detect highly toxic gases for environmental concern.

1. Introduction

Gas sensors are ideal candidates for environmental monitoring and their use becomes now more and more necessary in manufacturing industry for the detection of the leakage and diffusion of different toxic gases. This last decade witnessed the development of different types of gas sensors [1,2]. Most of them are metal oxide sensors [1], acoustic wave sensors (i.e., Quartz Crystal Microbalance (QCM) and Surface Acoustic Wave (SAW) [3–9], optical sensors [10–13], and chemiresistors [13–15].

The present challenge is the development of versatile and highly sensitive sensors for the detection of toxic pollutants, which are most of the time gas molecules at low concentration. Among the different principles of reading the sensitive film reaction, the gravimetric principle utilizing electroacoustic devices has been used around for years [16]. When used as an organic gas sensor, the resonator surface is coated with a sensitive layer which can react selectively to the sorption of gas molecules. As a result of the changed surface loading, the device changes its operation frequency. The principle of using acoustic wave mass sensitive transducers has initially been employed for thickness measurements of thin rigid films using QCM. Now QCM is a well established method for the measurement of small changes in mass based on the relationship between the mass loading of the surface of a quartz resonator and its resonance frequency [17]. Concerning gas sensing, most frequently thickness-shear oscillations in quartz AT-cut quartz plates are used because of their high-temperature stability and high quality factor. Nowadays polymer layers are found more suitable for QCM gas sensors due to the ease of their deposition (thin film can be easily obtained) and their cheapness [18,19].

In this work quartz AT-cut quartz resonators coated with polyurethaneimide (PUI) copolymers are designed in order to test the sensitivity towards two highly toxic organic substances – pyridine (C_5H_5N) and hexamethyleneimine, HMI, ($C_6H_{13}N$). Prolonged exposure to pyridine may result in liver, heart and kidney damage followed by coma and death. Pyridine's production and use as an industrial solvent and an intermediate in the production of vitamins, dyes, medicines and other organic compounds may result in its release to the environment through various waste

* Correspondence to: Institut Jean Lamour (IJL), UMR CNRS 7198, Universite de Lorraine, Department N2EV, Parc de Saurupt CS50840, 54011 Nancy, France.
E-mail address: Halima.alem@univ-lorraine.fr (H. Alem).

http://dx.doi.org/10.1016/j.talanta.2016.03.021
0039-9140/

streams. HMI is used as an intermediate in the synthesis of pharmaceutical, pesticide and rubber products. It is thus released to the environment through various waste streams from manufactures. To the best of our knowledge, there are only few literature works reporting on the development of selective layers for sensors for pyridine [18], while HMI sensitive layers appear to have not yet been reported.

This paper reports on a study of the response of AT-cut quartz resonators coated with polyurethaneimide (PUI) containing a controlled number of tertiary amine groups via the N-methyldiethanolamine (MDEA) group [20,21]. The response was analyzed in terms of gas chemical structure and polymer film thickness. The targeted application requires specific polymer properties and very good film forming ability for micro-sensor coating by a polymer nano-layer of at least 150 nm. The first part of the paper will thus focus on the polymer surface structure, which is critical for this micro-sensor application. The main features of PUIs thin films obtained by spin-coating will be described on the basis of atomic force microscopy (AFM) experiments. The latter technique will provide a first insight into the nano-structuration of the thin film surface which is expected to play a strong role in the targeted application. And finally the dependence of the resonator response on the gas chemical structure and polymer film thickness will be discussed.

2. Experimental section

2.1. Synthesis and deposition of the PUI film

Poly(urethaneimide) (PUI) backbone may bear amine groups by incorporating the N-methyldiethanolamine reactant. The synthesis process was completely described in a previous work [22] (for a brief description see Supp. Info.).

PUI thin films of ca. 100, 250, 500 nm were obtained by spin-coating of filtered PUI solutions at different concentration (% w/v), determined after a calibration line) in chloroform (Aldrich, HPLC grade) onto previously thoroughly cleaned electrodes which were used as model substrates for the targeted microsensors. The Süss-Microtec Delta 6 RC AK 256474 spin-coater was operated at a speed of 4.000 rpm with an acceleration of 3.000 rpm/s. The spin-coating time was 60 s. The thin films were thermally annealed at 60 °C for 2 h. The thickness of the polymer thin films was measured by a Dektat ST type mechanical profilometer with a vertical resolution of 1–2 nm.

2.1.1. Atomic force microscopy study

The morphology of the thin polymer films was characterized by atomic force microscopy (AFM) in intermittent-contact mode (Tapping mode) on a multimode Dimension Icon microscope (Bruker) equipped with a 100 μm close-loop scanner. Pointprobes NCHR probes (Nanosensors) were used. The cantilevers had a resonance frequency around 290 kHz and spring constant values around 40 N m^{-1}. The actual value of the spring constant was calibrated using the thermal noise method. Images were acquired in air at ambient temperature with a free vibration amplitude of 45–50 nm and an attenuation set-point of 0.8. At least three different zones were scanned on each sample and images at different magnification were acquired ($30 \times 30\ \mu m^2$, $10 \times 10\ \mu m^2$, $3 \times 3\ \mu m^2$ and $1 \times 1\ \mu m^2$). The images were treated and analyzed using home-made procedures developed under Igor Pro (Wavemetrics).

In intermittent-contact mode (Tapping mode), the cantilever is forced to vibrate at a frequency close to its resonance frequency [23,24]. When the tip approaches the sample surface, tip-surface interactions induce a shift of the resonance which corresponds to a variation of the vibration amplitude at the excitation frequency. In tapping mode, the tip intermittently taps the surface and the vibration amplitude attenuation is kept constant to access the surface topography. The phase-shift between the excitation signal and the cantilever vibration signal depends on the tip surface interaction forces: attractive forces lead to a negative phase shift, repulsive ones to a positive phase-shift. In tapping mode, when repulsive forces dominate, stiffer regions will present a larger positive phase-shift (brighter zones) and softer ones will present a smaller phase-shift (darker zones).

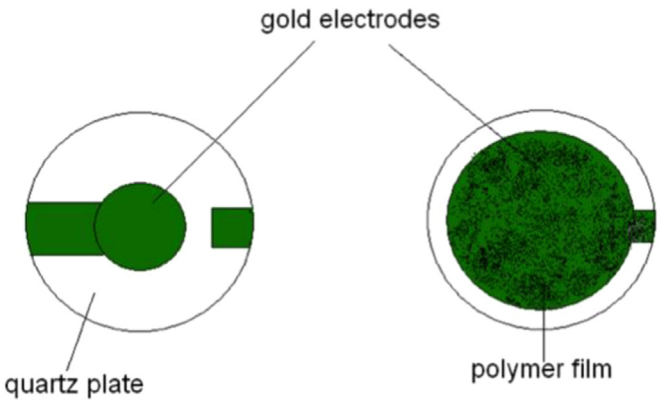

Fig. 1. Electrode configuration on AT-cut quartz resonator plate: (a) top face view; (b) bottom face view.

2.1.2. QCM study

AT-cut quartz resonators (courtesy of Piezoquartz, Sofia) have been used for the aims of this study. They oscillate in a thickness-shear mode with a displacement vector parallel to the plate surface. The conventional design of electrodes involved two contact pads on the top and bottom plate faces that served for both electrical connection and mounting. This arrangement was, however, problematic because of the insulating properties of the film, as polymer spin coating has to be done prior to contacting. To overcome such technological difficulties, we have used the arrangement shown on Fig. 1(a, and b) [25]. The bottom electrode covered almost the entire surface area with a contacting pad extending over to the topside. Thus the bottom side could be fully polymer coated and then the leads contacted on top upon clipping the plate. Increasing the bottom electrode area weakened the energy trapping effect and permitted a larger part of the plate to contribute to the resonance mass loading. The plates were 200 μm thick, with no plano-convexity, and 140 mm in diameter. Gold electrodes 200 nm thick have been coated as indicated in Fig. 1. The two electrodes diameters were 6.4 mm and 12.2 mm, respectively. The resonators were designed to operate at a fundamental resonance of 10 MHz. We applied the gas flow cell method developed in a previous work [26] to study the sensing properties of the PUI coated resonators. This analytic sorption method provides the use of an extremely wide variety of volatile organic liquids for which A, B and C Antoine's component-specific constants are known [27,28]; the capability for easily changing the vapor pressure (the concentration) of the volatile liquids with the temperature; as well as the accurate determination of adsorption characteristics of different materials in dynamic regime. So, the practical advantages of the method may be summed up in the following points: an opportunity for carrying out a variety of adsorption kinetic experiments under dynamic flow conditions at atmospheric pressure and ambient temperatures; the maintenance of constant adsorbate concentration during the sorption measurement; a relative operational simplicity, effectiveness, stability, applicability to different adsorption circumstances, etc.

This sorption method did not allow to precisely determine the