



An application of field-effect sensors for *in-situ* monitoring of degradation of biopolymers



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ABSTRACT

The characterization of the degradation kinetics of biodegradable polymers is mandatory with regard to their proper application. In the present work, polymer-modified electrolyte–insulator–semiconductor (PMEIS) field-effect sensors have been applied for *in-situ* monitoring of the pH-dependent degradation kinetics of the commercially available biopolymer poly(D,L-lactic acid) (PDLLA) in buffer solutions from pH 3 to pH 13. PDLLA films of 500 nm thickness were deposited on the surface of an Al–p-Si–SiO₂–Ta₂O₅ structure from a polymer solution by means of spin-coating method. The PMEIS sensor is, in principle, capable to detect any changes in bulk, surface and interface properties of the polymer induced by degradation processes. A faster degradation has been observed for PDLLA films exposed to alkaline solutions (pH 9, pH 11 and pH 13).

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1. Introduction

During the past years, biodegradable polymers have attracted a lot of attention from scientific community and industry. They replace more and more synthetic non-degradable polymers to minimize waste and enable new applications due to their specific property to disappear after a certain time. Especially, the biomedical sector has made use of these materials for novel applications, such as the controlled release of drugs [1–3], surgical implants [1,4], or scaffolds for tissue engineering [1,5,6]. Up to now, a great deal of effort has been already spent on the investigation of various classes of biodegradable polymers and blends of those with regard to their suitability (e.g., biocompatibility, mechanical properties, degradation period) for various applications. Although several polymers have made an enormous impact in biomedical research and clinical practice [7,8], there is a need for new biodegradable synthetic polymers with predicted biodegradability.

Since the kinetics of the degradation process of polymers is affected by various interacting processes within the polymer as well as in the surrounding environment (e.g., molecular weight,

diffusion, hydrophobicity, ionic strength, pH, temperature, etc), designing of polymers with predicted degradation kinetics is a complex process and requires numerous tests. Currently, a number of methods are available for the investigation of degradation processes of polymers, like the determination of the swelling and mass loss, the change of the molar weight characteristics, differential scanning calorimetry, scanning electron microscopy, etc [1,9–13]. Due to sample preparation and measurement routine, most of these techniques are laborious and not suitable for real-time or *in-situ* degradation monitoring. In addition, most of them use macroscopic polymer samples whose degradation kinetics was shown to be strongly dependent on the sample geometry because of diffusion aspects [14,15]. Degradation measurements on polymer monolayers using surface pressure–area isotherm measurements were shown to be suitable for real-time degradation monitoring [16,17]. However, since all cleavable bonds are in direct contact to the degradation medium, this technique separates the chain-scission process from transport phenomena involved in the degradation process, which is an important, rate-defining mechanism of “bulk degradation” – the prevailing mechanism of several widely-used biodegradable polymers. Furthermore, spectroscopic methods such as nuclear magnetic resonance or infrared spectroscopy offer the ability to monitor degradation processes *in-situ* [1]. However, due to the technical complexity and expensive equipment, they are not suitable for extensive studies examining a large number of samples.

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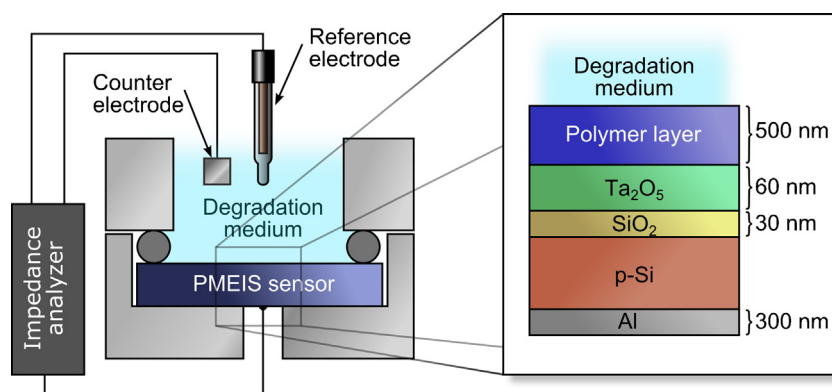


Fig. 1. Layer structure of the field-effect PMEIS sensor and schematic of the measurement set-up.

Recently, we introduced a polymer-modified capacitive field-effect electrolyte–insulator–semiconductor (EIS) sensor (further referred to as PMEIS sensor) as a novel and promising chip-based platform for *in-situ* monitoring of degradation kinetics [18]. In principle, this sensor is capable to detect any changes in the bulk, surface and interface properties, associated to thickness, coverage, relative permittivity of the polymer, and surface potential at or nearby the polymer surface induced by the degradation processes. Because of the possibility of direct electrical read-out, multiple sensors can easily be read-out in parallel, thus providing a higher throughput of measurements.

In order to control the degradability and predict the lifetime of polymer samples, a detailed knowledge about the degradation mechanism as well as the external factors influencing the degradation kinetics (e.g., pH value and ionic strength of the degradation medium, temperature) is essential. In the present work, field-effect PMEIS sensors have been applied for *in-situ* investigation of pH-dependent degradation kinetics of an amorphous poly(lactic acid) (PLA). PLA has shown an exceptional importance due to its biocompatibility and the fact that its degradation products can leave the human body via natural metabolic pathways. Currently, PLA is used in several medical devices and pharmaceutical applications approved by the United States Food and Drug Administration [19].

2. Materials and methods

2.1. Sensor fabrication and polymer deposition

Fig. 1 shows a schematic of the measuring setup and the layer structure of the PMEIS sensor. The PMEIS sensor consists of a silicon substrate (p-doped Si with an electrical resistivity of $\rho = 5\text{--}10\ \Omega\ \text{cm}$) covered with a double-layer gate insulator of $\text{SiO}_2\text{--Ta}_2\text{O}_5$ and a polymer film under investigation. The high-quality 30 nm thick SiO_2 is formed by means of dry oxidation of the silicon. The Ta_2O_5 layer of 60 nm thickness was prepared by electron-beam evaporation of 30 nm tantalum and subsequent oxidation to Ta_2O_5 . To complete the fabrication process of the EIS sensor, a 300 nm Al layer was deposited as rear-side contact. Finally, the wafer was separated into single chips with sizes of $10\ \text{mm} \times 10\ \text{mm}$, which were further covered with the polymer layer. More details on the fabrication of EIS sensors are provided in [20,21].

In the present study, the commercially available poly(D,L-lactic acid) (PDLLA, RESOMER[®] R 202H, 50:50 ratio of D/L-lactic acid, Evonik Röhm GmbH, Germany) with a molar mass in the range of $M_w = 10,000\text{--}18,000$ was used as a model polymer. It consists of the two enantiomers L- and D-lactic acid in a syndiotactic arrangement and is therefore, amorphous. Since PDLLA belongs to the group of aliphatic polyesters, its ester group is biodegradable by hydrolysis. Compared to the polymers composed of only

one monomer unit (either L- or D-lactic acid), samples made from PDLLA have a much shorter lifetime offering their application as carrier matrix in controlled drug-release systems.

A thin layer of PDLLA with a thickness of $500 \pm 30\ \text{nm}$ was deposited on top of the sensor from the polymer solution of 90 mg/mL by means of a spin-coating method. To dissolve the polymer, methyl ethyl ketone was used. In a previous study [18], the relation between the polymer layer thickness and the polymer concentration in the solution was investigated by means of profilometry measurements. Based on these experiments, the reproducible preparation of polymer layers of desired thickness could be achieved by adjusting the polymer concentration in the solution.

2.2. Functioning principle

Due to the space-charge region close to the semiconductor–insulator interface, capacitive field-effect sensors exhibit a variable capacitance that depends on the potential distribution between the bulk of the semiconductor and the electrolyte solution. By an externally applied DC (direct current) voltage, the device can be biased to specific regions (accumulation, depletion and inversion) of its capacitance–voltage ($C\text{--}V$) characteristic. The typical shape of the high-frequency $C\text{--}V$ curve of a bare p-type EIS sensor, as well as of a PMEIS sensor, is schematically depicted in Fig. 2. As can be seen, the presence of an additional polymer layer shifts the $C\text{--}V$ curve of the original EIS structure along both the capacitance and the voltage axis. The shift of the $C\text{--}V$ curve along the capacitance axis is due to the additional capacitance of the polymer layer and the shift along the voltage axis can be attributed to the difference of potentials at the electrolyte/gate-insulator and electrolyte/polymer interfaces, respectively. The detailed description

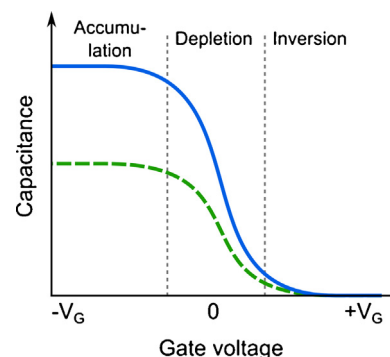


Fig. 2. Typical shape of high-frequency $C\text{--}V$ characteristics of a p-type EIS (solid line) and a PMEIS sensor (dashed line).

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