

# In situ infrared ellipsometric monitoring of the growth process of polyaniline thin films and doping with poly(4-styrenesulfonate)



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## ABSTRACT

In this work, different undoped and doped polyaniline (PANI) films were synthesized by electrochemical pulse deposition. The growth process was in situ investigated using a combined infrared spectroscopic ellipsometry (IRSE) and optical spectroscopy set-up in the visible spectral range [Vis-ellipsometry and reflectance anisotropy spectroscopy (RAS)]. A growth acceleration effect and thicker PANI films in the presence of poly(4-styrenesulfonate) (PSS) are concluded from the measurements in the infrared and visible spectral range. IR-microscopic spectra revealed a strong inhomogeneity of the obtained PANI film doped with PSS. Moreover, the interpretation of the in situ IR ellipsometry spectra not only delivered qualitative (e.g., chemical structure and composition) information, but also quantitative information (e.g., film thickness) in the growth process of the PANI films by applying an optical layer model.

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## 1. Introduction

Since the discovery of first electrical conductive conjugated polymer (polyacetylene) in 1977 by Shirakawa, Heeger and MacDiarmid, the conducting polymers attract more interests in both academic and practical research areas because of their potential applications in clean energy, sensors and microelectronic devices, and especially in organic solar cells (OSC) and organic light emitting devices (OLEDs) [1,2]. Electrochemical synthesis of conducting polymers is one of the most common and convenient method, which provides the capability to grow the films by precise control of the electro-polymerization charge and to achieve desired composition and materials property control by electrophoretic blending with other non-redox-active polymers. Among those conducting polymers, polyaniline (PANI) is most promising because of its relative ease synthesis, low cost monomer, tunable electrical conductivity and better stability in the environment [3]. However, the main disadvantages of the conducting polymers including PANI are inherent lower conductivity compared to metal and poor solubility in all solvents. The properties of conducting polymers can be improved or modified by using selected dopants. The

preparation, mechanism of polymerization, processing and application of PANI films were already well reviewed in several papers [4–7]. In this work, the focus of interest is the in situ study of the growth and doping of PANI thin films, which could be employed as conducting and absorbing layer for OSC and OLEDs applications [8].

Non-destructive, highly sensitive methods for in situ monitoring in aqueous environments are required for studying of deposition processes of thin organic films (e.g., deposition kinetics), optimization of the deposition parameters (e.g., variable pH value, temperature, voltage), controlling and improvement of the thin films properties (e.g., thickness, optical properties, homogeneity), and studies of the adsorption or desorption of molecules at the liquid/solid interface. In such studies optical spectroscopy is often used as non-invasive and contactless method. In particular vibrational spectroscopic methods like Raman spectroscopy or infrared spectroscopy [e.g., infrared spectroscopic ellipsometry (IRSE)] offer the possibility to verify the chemical composition and to investigate the microscopic structure by interpretations of the measured spectra. Due to the different interaction mechanism a quantitative evaluation of Raman spectra (including resonant Raman, surface-enhanced Raman scattering or tip-enhanced Raman scattering) is typically more complex than that of IRSE. On the other hand for in situ spectroscopy in the mid-IR spectral range (wavelengths from about 2.5 to 25  $\mu\text{m}$ ) the penetration depth of radiation in water

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is several tens of micrometers only. This fact gives strong restrictions for the design of an in situ cell often involving a geometry with infrared transparent substrates. However, many technology relevant problems in silicon technology can in principle be studied with the use of low doped IR transparent silicon substrates. When attenuated total reflection (ATR) geometries [9–11] with multiple internal reflections or specific geometries of the ATR Si prisms were used, usual the accessible spectral range and depolarization along the optical path in the prism material are limiting factors. These drawbacks are overcome with the used single reflection geometry of the wedge (below the ATR regime) for which the length of the optical path is small and multiple reflections are suppressed. In general from interpretation of the measured IR spectra the microscopic and chemical structure of the film can often only be revealed together with complementary results from other experimental methods like vacuum ultraviolet–visible ellipsometry [12,13], X-ray photoelectron spectroscopy [14], scanning microscopy (e.g., atomic force microscopy [15] or scanning near-field infrared microscopy [16,17]). Compared to classical in situ IR measurements, the technical advantages of an ellipsometric measurement are that it sensitively determines absolute measurement parameters and in addition, it can minimize the atmospheric contributions if the single intensity measurements are performed in quick order. Then the contributions from H<sub>2</sub>O vapor in the ellipsometric spectra are minimized because they are determined from intensity ratios  $\Psi = \sqrt{r_p/r_s}$ .

A standard method in the UV–vis spectral range for studying thin organic films is in situ Vis spectroscopic ellipsometry [18,19]. Evaluation of spectra with optical layer models can deliver film thicknesses, refractive indices, composition and electronic properties. If ellipsometry [20] is performed at zero degree incidence angle it is methodically similar to the so-called reflection anisotropy spectroscopy (RAS) used in this work. Compared to conventional reflectance measurements, RAS monitors the anisotropic properties of surfaces, interfaces and doping-induced surface electric fields, which makes it a unique optical in situ technique [21].

In recent years we already consecutively used RAS and IRSE in a similar set-up for various in situ characterizations e.g., of polyelectrolyte brushes [22,23] or of deposition of polypyrrole [24]. The results in this work show that from IRSE not only the qualitative information (e.g., chemical composition of the PANI films, dopants) can be achieved, but also the quantitative information (e.g., film thickness) in the growth process.

## 2. Experimental

### 2.1. Materials and chemical reagents

The substrates used in the experiments were infrared transparent, double-side polished Si(1 1 0) wedges (1.5°) with thin native oxide layer (Vario GmbH, Wildau, Germany). The used wedges were first cleaned in piranha solution [H<sub>2</sub>SO<sub>4</sub> (98%, BASF): H<sub>2</sub>O<sub>2</sub> (30%, BASF) = 3:1 (v:v)] for 10 min to remove the organic contaminants. After extensive rinsing with water, the cleaned Si substrates were put into the HF (5%, BASF) for 0.5 h and achieved the H-terminated surfaces for the following electrochemical deposition.

The aniline (99.5%+, Sigma–Aldrich) was used as received and freshly distilled before starting the deposition. The concentration of the aniline was 0.3 M in diluted aqueous H<sub>2</sub>SO<sub>4</sub> [0.1 M] solution, which was purged by dried N<sub>2</sub> for 15 min to remove the dissolved O<sub>2</sub> in the solution before starting the deposition. As dopant, 0.1 g poly(sodium 4-styrenesulfonate, PSS) [–CH<sub>2</sub>CH(C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>Na)–, Sigma–Aldrich, M<sub>w</sub> ~ 70,000] was added into a part of the prepared aniline solution (about 150 ml). All aqueous solutions were prepared using highly purified water (18.2 MΩ cm,

25 °C). The molecular structure of aniline and PSS is shown in Scheme 1.

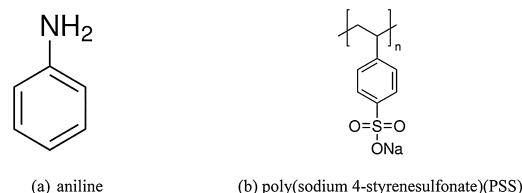
### 2.2. Electrochemical polymerization process

The polymerization was performed with pulsed potentiostatic method and the used parameters are as following: the oxidation of aniline monomer was performed at +2.3 V for 100 s and interrupted at –0.75 V for additional 100 s (1 loop). The whole process lasted for 50 loops. In all steps of the preparation process the solution was pumped in a cycle from a reservoir through the flow-cell.

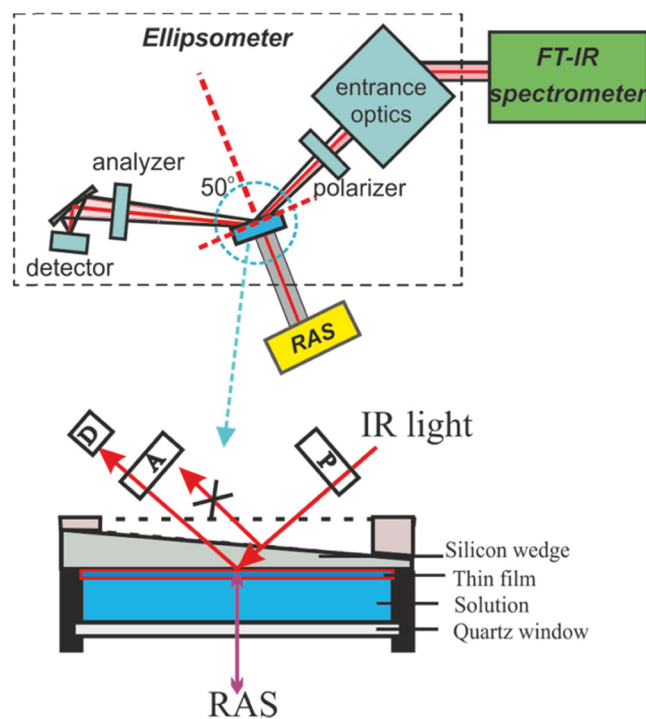
### 2.3. Spectroscopic methods

The growth process of a PANI film on a Si(1 1 0) surface was in situ monitored using the combined experimental set-up as shown in Scheme 2. Details for the geometry for the IR measurements can be found in Refs. [22,23]. The change of the contribution of the intrinsic Si(1 1 0) substrate anisotropy was monitored using Epi-RAS TT (Laytec AG, Germany) during the deposition process. Due to the absorption of the deposited PANI in the VIS spectral range a decreasing RAS signal is observed with ongoing deposition process.

The polarized in situ IR measurements were performed on a custom-build ellipsometric set-up after 10, 20, 30, 40 and



Scheme 1. Molecular structure of used aniline monomer (a) and PSS dopant (b).



Scheme 2. Schematic drawing of the combined in situ IRSE and RAS set-up (on top) and the used electrochemical cell with the pathway of the light for IRSE and RAS measurements (D: detector; P: polarizer; A: analyzer; working electrode is the Si(1 1 0) wedge) [24].

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