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Development of a Combined pH- and Redox-Sensitive Bi-Electrode Glass Thin-Film Sensor

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Abstract:
A combined pH- and redox-sensitive bi-electrode glass thin-film sensor has been developed for the simultaneous detection of pH and redox potential in aqueous solutions for the first time. The pH- and redox-sensitive glass bulk materials have been prepared and tailored by glass-pouring processes. The electrode structure (sensor chip) is fabricated via conventional thin-film techniques on glass substrate. The glass bulk materials were transferred on the electrode structures by means of pulsed laser deposition technique. The fabricated sensors have been characterized physically and electrochemically by scanning electron microscopy (SEM), Rutherford backscattering spectroscopy (RBS), profilometry, energy dispersive X-ray spectroscopy (EDX), impedance and potentiometric measurements.

Key words: redox glass, pH glass, bi-electrode thin-film sensor, potentiometry, pulsed laser deposition

Introduction

There is an increasing demand for miniaturized sensors for the simultaneous detection of pH and redox potential in aqueous solutions. Those sensors have to be cheap in fabrication but should have advanced performance and handling characteristics with respect to commercial pH-glass- and redox electrodes. Thereto, in this work siliceous glass targets have been developed and deposited via pulsed laser deposition (PLD) technique onto thin-film electrode structures. Especially, in case of the redox-active sensor part, where often noble metals (e.g., Pt, Pd, Au) are used, the alternative of a glass-based electrode might be beneficial: it is known that Au electrodes respond to chlorides and cyanides under certain circumstances; Pt and Pd surfaces contaminate by different catalytic poisons, proteins etc. and Pt can act as catalyst in certain media [1]. The usage of special glasses for measuring the redox potential is already demonstrated in different approaches. At the same time, there have been pH-glass-shaped electrodes, fabricated by glass blowers [2] which is only possible with certain glass compounds. A further approach have been coated-wire electrodes [3] but with a high failure rate because of different linear thermal coefficients of expansion between electrode and shaft glass. Recently, a redox-sensitive glass thin-film electrode is fabricated by conventional thin-film technology together with PLD technique [4]. In the present work, such thin-film sensors are optimized and are, for the first time, combined with a thin-film pH-glass- and redox electrode as a bi-electrode sensor for the simultaneous detection of pH and redox potential in aqueous solutions.

Glass preparation

As a part of optimization of suitability for the PLD process as well as sensor behavior, a variety of glass compositions for pH- and redox-sensitive glasses, respectively, have been synthesized. The different mixing ratios have been sintered at 1400 °C and poured in a pre-heated mold as glass targets.

Sensor fabrication

The transducer structure was fabricated on glass substrates. The chosen glass substrate has comparable physical properties as the pH- and redox-sensitive glasses, which enhances the stability of the later deposited glass thin films. The metal conducting lines and electrodes were deposited via electron-beam evaporation and patterned by conventional photolithography and lift-off process. For the electrodes stacks, Pt on top of Ti (Ti/Pt) and Au on top of Cr (Cr/Au), have been used (see Fig. 1, fabricated Pt transducer structure).

Pulsed laser deposition

The glass targets (see sections "Glass preparation") were mounted into the vacuum chamber of the PLD system: a KrF excimer laser with repetition rate of 10 Hz, pressure of 2 x 10^{-2} hPa O_2-atmosphere and 300 °C, respectively. Thereby, a plasma was generated, from which the glass material was deposited on the transducer structure. A scheme of the PLD setup is depicted in Fig. 2.

Fig. 1. Photograph of Ti/Pt transducer structure (chip size: 10 mm x 20 mm) fabricated by thin-film technology (left: pH-sensitive area, right: redox-sensitive area).

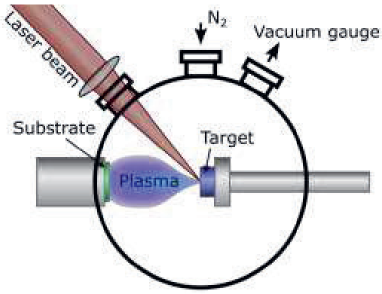

Fig. 2. Schematic of the on-axis PLD process.

After deposition of the sensitive thin-film glasses, the chips have been glued onto a printed circuit board and encapsulated with an epoxy material.

Experimental

The sensors have been characterized physically as well as electrochemically. Scanning electron microscopy (SEM) examinations have shown homogeneous and dense thin-film glasses deposited on the electrode surface. By means of RBS and EDX measurements the glass layer composition has been evaluated and confirmed a good transfer of the bulk glass material into the thin-film state via PLD. Profilometry allowed to determine the thickness of the deposited thin-film materials.

The electrochemical characteristics of the bi-electrode sensor result in a functionality of both the pH-and redox-sensitive sensor part (see also Fig. 1).

Fig. 3 shows a typical calibration curve of the pH-sensitive part of the bi-electrode sensor.

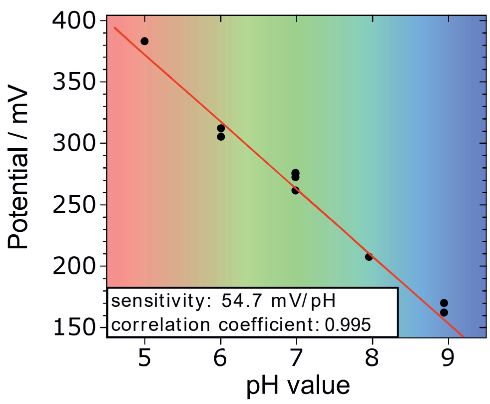

Fig. 3. Calibration curve of the pH-sensitive part of the thin-film electrode.

The sensor possesses an average pH sensitivity of 54.7 mV/pH, which is close to the theoretical Nernstian value at room temperature (RT). The measurements were conducted in buffer solution at RT for 5 min at each pH value.

The characterization of the redox-sensitive part of the bi-electrode was done in KHCF(III)- and KHCF(II)-solution in different mixing ratios (2:1, 1:2). The measurement in Fig. 4 clearly shows the different redox potentials of the two calibrated analytes.

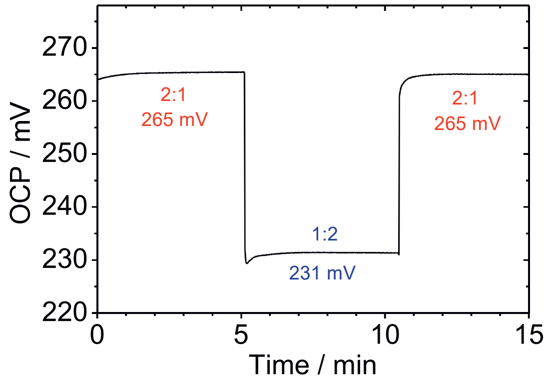

Fig. 4. Measurement curve of the redox-sensitive part of the thin-film electrode. OCP: open circuit potential.

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