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Development of redox glasses and subsequent processing by means of pulsed laser deposition for realizing silicon-based thin-film sensors

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ABSTRACT

In this work, two different redox-sensitive glass materials have been fabricated for the development of a production friendly redox electrode. The specific glass targets have been prepared by glass pouring process. The transducer structure is fabricated via conventional silicon-based semiconductor technology. The glass bulk material was deposited for the first time by means of pulsed laser deposition process into the thin-film state on the sensor structures. The fabricated sensors have been physically and electrochemically characterized by X-ray photoelectron spectroscopy, determination of expansion coefficient, impedance and potentiometric measurements.

1. Introduction

As it is known, precious metal-based redox electrodes under certain operating conditions possess several drawbacks concerning their measurement performance. For example, it makes a difference whether gold or other noble metals are used as redox-sensitive membrane materials. Furthermore, under certain circumstances gold electrodes additionally respond to chlorides and cyanides. Platinum and palladium form hydrides in reducing solutions. Both electrodes become unusable when catalytic poisons, e.g., SO_2 or other sulfur compounds, contaminate their surface. Also proteins cause inactivation of these noble metal surfaces and the presence of several gases influence the half-cell potential of such electrodes. Especially, platinum can act as catalyst in certain redox media [1].

An alternative to conventional redox probes without most of the above-mentioned drawbacks is represented by electrodes based on electron-conducting glasses [2], which contain iron or titanium oxides in different oxidation states. Here, the electron-hopping process between different metal oxides of the same metal causes the electrode function [3]. Moreover, the electronic conductivity of related glasses is four orders of magnitude larger than the ionic component of conductivity [4].

Constructional particularly two main embodiments of glass-based redox sensors were described, hitherto: On the one hand, there are rod-shaped all solid-state electrodes, which in analogy to conventional pH-glass electrodes have an electrode membrane fabricated by a glass blower (Fig. 1a) [5]. On the other hand, recently, planar redox-glass electrodes with sensitive membranes on ceramic substrates have been presented (Fig. 1b) [6]. In total, with regard to the first mentioned embodiment it can be ascertained that only in exceptional cases a processability of the special glasses by the glass blower is given. The same applies to the electrode shape (coated-wire electrode) according to Fig. 1c, we have slightly modified currently [7]. In addition, there are high failure rates for both electrode types because of different linear thermal coefficients of expansion between electrode and shaft glasses.

The fabrication of thick-film electrodes in this connection is a preferred manufacturing possibility. In the course of the paste preparation, however, the amorphous character of the membrane materials is partially lost (e.g., by grinding processes, by addition of binder). As it is shown in Fig. 2 with X-ray diffractometry measurements, crystalline phases, e.g., magnetite could be detected in the screen-printed thick film of the redox glass and is thus, prone to glass corrosion.

It is, therefore, the objective of this work to come to glass based, production friendly redox electrodes. For this purpose, the pulsed laser deposition (PLD) technique as efficient thin-film technology will be applied in order to fabricate thin-film redox glasses for the first time. It was recently demonstrated that the PLD technology is a very attractive tool to deposit thin-film materials for chemical

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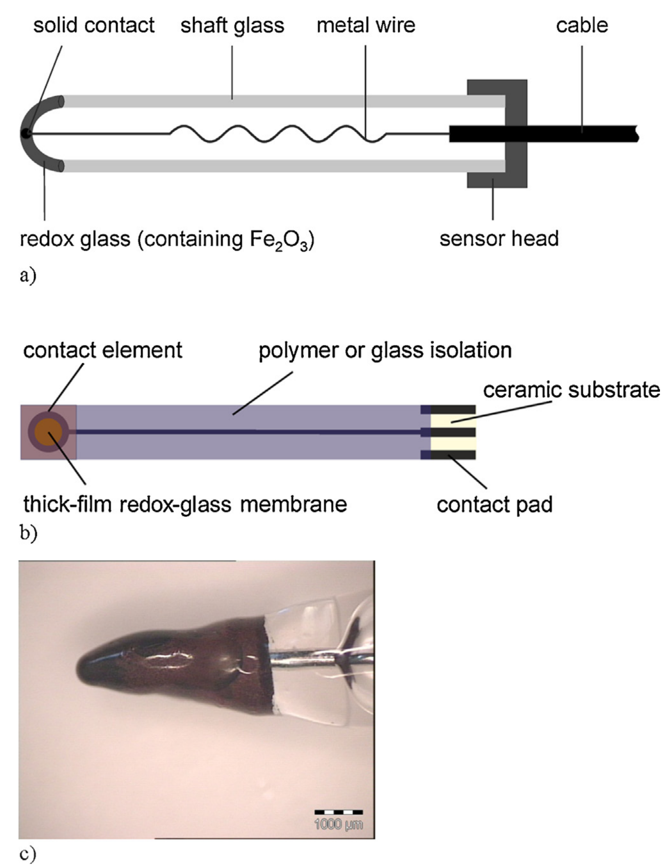

Fig. 1. Glass-based redox electrodes in (a) conventional shape of pH-glass electrodes, (b) as thick-film electrode, and (c) as coated-wire electrode.

sensing in liquids: PLD-prepared Al_2O_3 layers (~50 nm thick) serve as pH-sensitive materials [8]. Moreover, chalcogenide glass materials with layer thicknesses of about 500 nm have been successfully applied for heavy metal analysis; examples are potentiometric copper, cadmium and thallium sensors [9] or cadmium sensors based on different field-effect devices [10] as well as sensor arrays [11], or sensor arrays together with artificial intelligence/fuzzy logic [12]. A general survey on chalcogenide glass based sensors and (micro-)electrodes can be found in [13]. In order to realize redox-sensitive layers, thereto, sensitive glasses were developed and

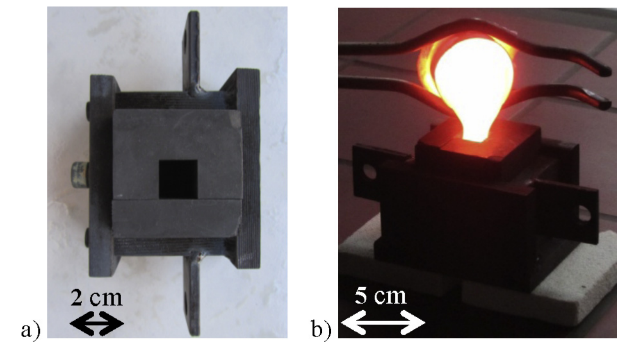

Fig. 3. Photograph of the two-piece graphite mold (a) and of the glass pouring process (b).

characterized and afterwards processed to targets for the subsequent PLD deposition onto photolithographically patterned silicon chips with electrode structures [14]. The PLD process itself has to be further developed for this special application; first results with these redox-sensitive thin-film sensors will be presented in this work.

2. Experimental

2.1. Glass preparation

The authors have synthesized a variety of redox glasses [6]. For the presented results the glasses of type A and B have been chosen. Their properties had been the most suitable for the fabrication of targets for the PLD process. Both glasses consisted of SiO_2, Fe_2O_3, Li_2O und Na_2O (Table 1). They differed in the composition of the amount of alkali metals. Glass A incorporated more Li (y) than glass B, meanwhile glass B contained more Na (x). The sum of both alkalis remained constant in both glasses ($x + y$ = constant).

For the preparation of the redox glasses homogeneous batches of SiO_2, Na_2O (inserted as Na_2CO_3), Li_2O (inserted as Li_2CO_3) and Fe_2O_3 of different mixing ratios were given in a covered platinum crucible and sintered at 1400 °C in a high-temperature chamber furnace.

The molten glass was then poured in a two-pieces mold made of graphite (Fig. 3), which is arranged in a retainer. The mold has the exactly defined dimensions required for the fabrication of the

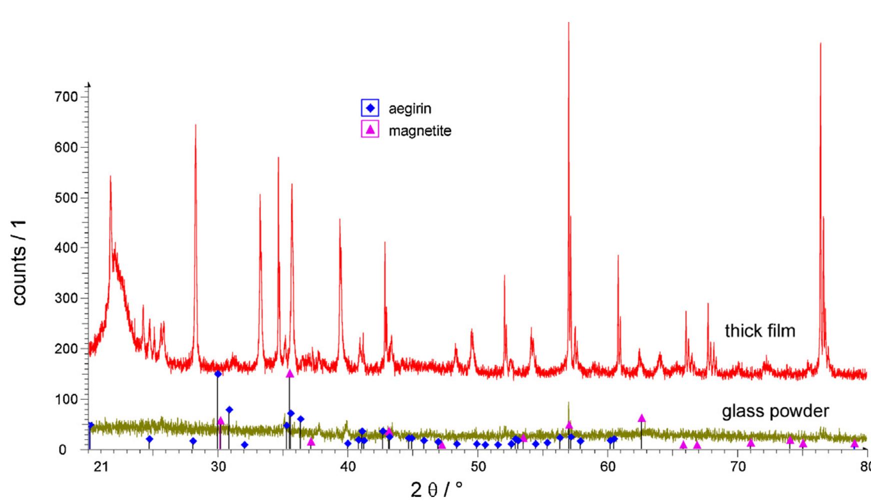

Fig. 2. XRD diffractogram of glass A for redox electrodes in the different processing states; powder (yellow) and thick film (red). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)