PLD as a new technology for the fabrication of pH glass based planar electrochemical sensors

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***Abstract*—Traditionally sensitive silicate membranes for pH electrodes are fabricated by glassblowers. Recently, because of a more effective fabrication in certain cases, also so-called blowing machines are in use. In this way neither miniaturization nor a planar arrangement of the sensors can be realized. Pulsed laser deposition (PLD) could provide ideal conditions to reduce the above-mentioned drawbacks. In this contribution, the first results of using this technology for the fabrication of planar glass based electrochemical pH sensors are demonstrated, whereby the characterization of the amorphous silicate glass before and after the PLD process is in the focus of this article.**

Keywords- electrochemical sensor; pulsed laser deposition; planarity; sensor miniaturization; thin film; pH measurement; SEM; XPS; µ-RFA; EIS.

I. INTRODUCTION

Sensitive membranes are essential functional components of potentiometric chemo sensors. In this respect, according to Figure 1, a distinction is made between solid-based and liquid membranes.

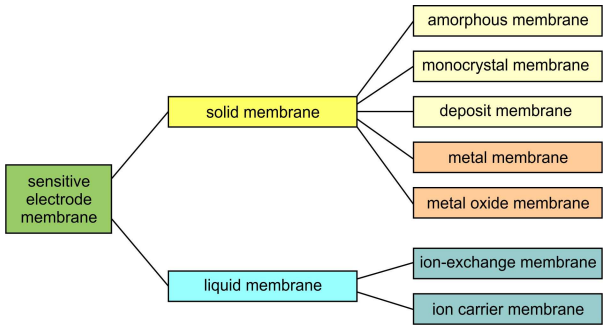

Figure 1. Classification of membrane materials for electrochemical sensors

Amorphous glass materials, which can be realized in different ways [1, 2], play a significant role for the fabrication of solid membranes. The reason is that especially the pH determination, which is one of the analyses performed most frequently worldwide, is carried out with electrochemical electrodes based on such membranes according to standards [3]. The membrane materials used here are silicate glasses with high ionic conductivity, which are mainly achieved by using alkaline as well as alkaline earth metal oxides, changing the silicate glass network [4] like it is shown in Figure 2.

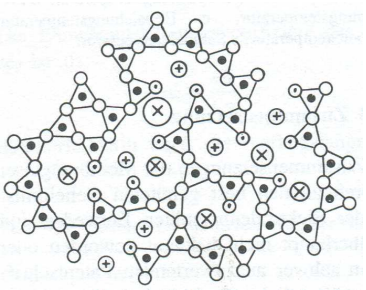

Figure 2. Two-dimensional structure of a silicate glass with network changing components
• Si, o oxygen bridge, Θ separate oxygen, ⊗ network changing component, ⊕ cation

Silica based electrode glasses, as a rule, are generated by melting their basic materials in covered platinum crucibles for several hours at temperatures > 1300 °C. For the further processing by the glassblower it is useful to outpour the liquid glass material, e.g., in a graphite flume. In this way, rods of the special glass are obtained. From these, glassblowers for the most parts produce basket or dome-shaped conventional pH electrodes in quantities of several million pieces per year. They contain a buffer solution and an electrochemical reference system (as a rule an electrode of 2nd kind) in its interiors. Modifying the glass composition makes it possible to realize similarly constructed silicate glass based electrodes with sensitivities for a number of other cations, mainly of metals of the first group of the periodic table [5].

Beside the above mentioned sensors, whose functionality is based on ionic conductivity, there are also probes with electron conducting amorphous glass membrane materials. These include redox glass [6] and chalcogenide glass electrodes [7]. For both types of electrodes the selection of an optimal internal reference system is relatively simple. As a result of the predominant electron conductivity of the sensitive membrane materials a direct contact of the special glasses with a (noble) metal is appropriate.

Therefore, liquid system components are not applicable for chemo sensors based on such materials. From constructional point of view, on the one hand, it is possible to fabricate compact electrodes by sticking a wire directly on the surface of the functional amorphous body, e.g., using a conductive varnish (see Figure 3); on the other hand, it is also possible to form a thin metal coating directly on the electron conducting glass by electro-plating (see Figure 4).

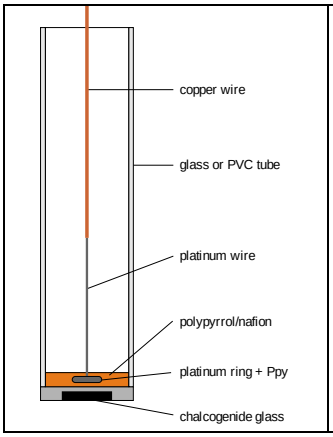

Figure 3. Schematic drawing of a chalcogenide glass electrode [8]

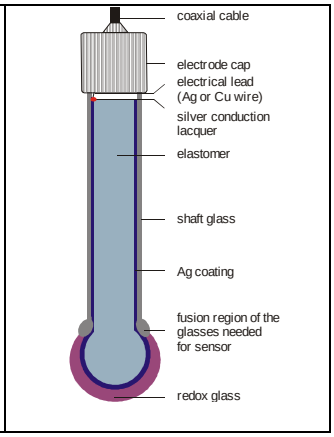

Figure 4. Schematic drawing of a redox glass electrode [9]

Also, for silicate glass based cation selective electrodes it is an interesting task to replace the common liquid system components by solids due to the purpose of their application. The functionality causing ionic conductivity of siliceous pH- but also pLi-, pNa or pK-glasses [10] requires an interlayer with mixed electrical properties on the reverse side of the sensitive membrane. A transition from an ionic conducting material to an electronic conductor (e.g., metal) may lead to a so-called blocked interface and consequently to an unfavorable measurement behavior [11].

In the past, several suggestions were made to realize such interlayers. In the context of the investigations presented here, the possibility to form thin layers of zinc oxide or titanium oxide between sensitive glass and a noble metal should be mentioned [12]. Previous work on all solid state glass electrodes was concerned with sensors fabricated with precision manufacturing techniques and screen printing (see Figure 5). Here, a clear stabilization of the half-cell potentials over the time could be obtained compared to a direct metal contacting [13, 14, 15].

PLD as a preparation method for sensors used in electrolyte containing liquids has still not become widespread. Today the PLD technology is particularly used for the deposition of diamond-like carbon layers (DSL) in order to improve the surface properties of highly stressed tools and components [16]. For the application in optoelectronics and chemical sensors, chalcogenide films were prepared by pulse laser deposition [17, 18, 19]. In the following it is reported on investigations using PLD as fabrication technology to realize planar all solid state pH glass electrodes according to a layer design described above. Beside the realization of an adherent metallic basic electrode on a substrate, special attention will be focused on the stoichiometric deposition of the functional sensor material from a prefabricated glass target by laser ablation. There should be no material loss during the PLD process as described in literature, e.g., for the synthesis of bio glass thin films [20].

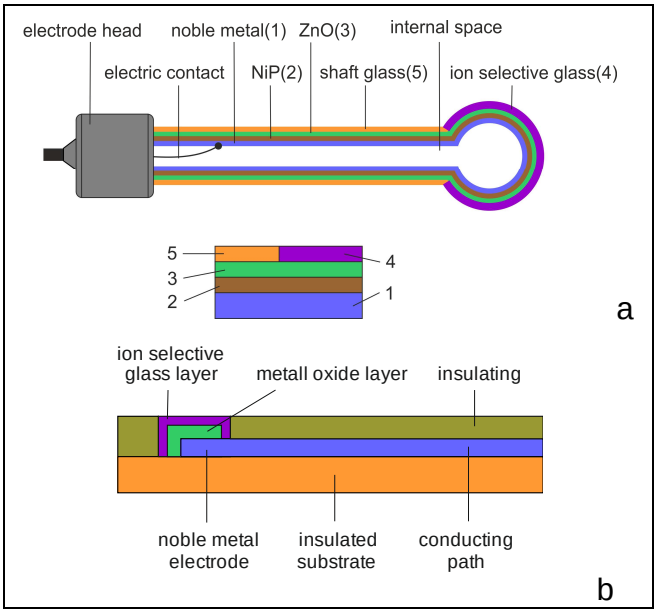

Figure 5. All solid state pH glass electrodes based on ZnO as interlayer
a fabricated in fine and glass mechanics according to [14]
b fabricated in thick film technology according to [15]

In Section II, the fabrication of the glass targets, the PLD process for the glass layer deposition and the characterization of these layers are described. Results of scanning electron microscope investigations, micro-X-ray fluorescence analysis, X-ray photoelectron spectroscopy and electrochemical measurements are presented in Section III.

II. EXPERIMENTAL

A. Fabrication of the glass targets

The targets of the sensitive pH glasses for the PLD process are obtained by pouring the molten glass in a preheated graphite mold according to Figure 6a. This manufacturing method delivers homogeneous and also amorphous target materials with defined geometries. According to Figure 6b, the glass cylinders were fabricated and singularized in discs with a thickness of 5 mm by means of a precision saw (Accutom-50, Fa. Struers GmbH, Willich, Germany). To improve the mechanical stability the

glass rods were embedded in an epoxy resin and fixed on the target holder for the PLD process (Figure 6c).

a) Pouring of molten glass in a graphite mold

b) Targets of pH glass

c) pH glass target fixed on target holder

Figure 6. Fabrication of the glass targets

B. PLD process

The preparation of the thin sensory functional layers was carried out by sputtering methods and PLD. For this purpose, a combined coating system CREAMET 500 PLD S2 (Creavac Vacuum Coating Technology GmbH, Dresden, Germany) was used, which provides both deposition processes (see Figures 7 and 8). Furthermore, a simultaneous substrate and mask handling is possible without an interruption of the vacuum during the coating process.

Figure 7. Combined coating system with PLD (1) and sputter (2) chamber

With integrated substrate handler and mask change system, two sputter targets, six PLD targets and altogether five changeable masks can be used and combined for the process.

As substrates pre-cleaned glass plates consisting of soda-lime glass with a size of 50 mm x 15 mm and a thickness of 1 mm were used. They were pretreated with the initial plasma process at a chamber pressure of 3.0×10^{-2} mbar under an argon atmosphere. As chamber pressure for the following sputtering processes of the adhesive layer (Ti) and the electrical conducting noble metal electrode (Au or Pt) a value of 7.0×10^{-3} mbar was used.

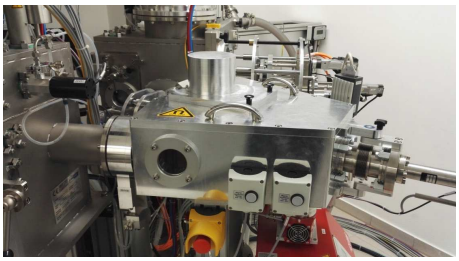

Figure 8a. Transfer device with mask and substrate handler

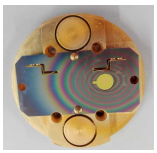

Figure 8b. Substrate holder with changeable mask

After finishing the sputtering processes the coated substrates were removed and the masks were changed in a so-called „Load-Lock-Box“. Prepared in this way, the substrates were transferred into the PLD coating chamber using a carrier and the PLD process was started.

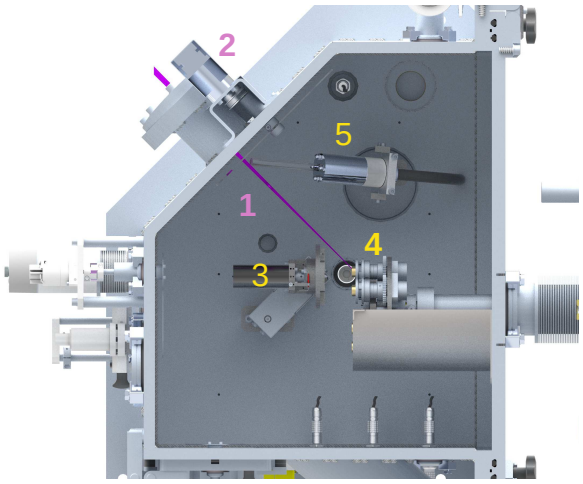

Figure 9. Construction of the PLD chamber

1 laser beam (KrF 248 nm) 2 laser power meter
3 substrate holder 4 target holder
5 ion source

The deposition of the thin pH glass films was conducted by a KrF excimer laser source (ComPexPro 110, Coherent LaserSystems GmbH & Co. KG., Göttingen, Germany) using a wave length of 248 nm, a fluence of 5.6 J/cm^2 at pulse lengths of 20 ns and a pulse frequency of 10 Hz. The determination of the laser power before and after the coating process in connection with a periodical cleaning of the entry window ensured long-term stable and reproducible basic conditions. The PLD process was carried out at a chamber pressure of 3.1×10^{-7} mbar in a N_2 atmosphere. The substrate was kept at room temperature. As ablation time of the sensitive layers a period from 10 to 30 minutes was selected. The substrates were positioned perpendicular to the plasma (On-Axis-PLD) (Figure 9).

C. Characterization

Physical Characterization

The energy dispersive micro-X-ray fluorescence analysis (µ-RFA) system M4 Tornado (Bruker Nano GmbH, Berlin, Germany) was used for the position-sensitive chemical elemental analysis. It allows the analysis of large and inhomogeneous samples as well as smallest particles fast and at low vacuum under environmental conditions.

In order to obtain information on the morphology, the surfaces of the prepared *pH glass thin films* were examined using the scanning electron microscope Helios 660 (FEI, Eindhoven, Netherlands).

X-ray photoelectron spectroscopic (XPS) data were acquired with the system SAGE HR 100 Compact High Resolution (company SPECS Surface Nano Analyses GmbH, Berlin, Germany) using non-monochromatised $Mg_{K\alpha}$ radiation (hν=1253.6 eV) with 12.5 kV and 250 W beam settings at a pressure of $2x10^{-8}$ hPa in the analysis chamber. With XPS it is possible to determine the chemical composition of the uppermost atomic layer of a material surface, because low beam energy (12.5 kV) is applied. Other radiographically methods (e.g., like µ-RFA) require beam energies up to 50 kV; elements from the volume will also be detected.

In addition to the described usage of µ-RFA and XPS, which allow statements about bulk properties of the target materials and adsorptive contaminations as well as surface effects, it is also possible to use energy dispersive X-ray analysis (EDX) and x-ray diffraction (XRD) as further radiographically research methods. Their application by means of the systems QUANTAX 400 D on FEI Helios 660 with two XFlash® 6 detectors (Bruker Nano GmbH, Berlin, Germany) (EDX) and D8 Discover High-Resolution Diffractometer (Bruker AXS GmbH, Karlsruhe, Germany) (XRD) show that amorphous sensor glass membranes can be realized using PLD as thin film production method.

Electrochemical Characterization

Electrochemical impedance spectroscopy (EIS) is an approved method for the characterization of resistance changes of systems with ion-sensitive glass membranes even for high-impedance and easily polarizable systems, which are present in pH glass electrodes.

In [21], EIS investigations on glass-metal transitions were carried out. Vonau et al. [22] used this method in combination with concentration analysis studies to describe the change in the pH properties of traditionally produced pH glass electrodes as a function of the duration of the application and the temperature and to elucidate their causes. Impedance spectroscopic methods were used to demonstrate the successful deposition of a glass layer by means of PLD technology on a sensor structure.

On the basis of the determined impedance values (frequency-dependent alternating-current resistors), the electrical conductivities of the PLD thin films could be estimated.

The impedance spectra were recorded using a measurement system Gamry Interface 1000 (Gamry Instruments Inc., Warminster, USA) in different buffer solutions according to the suggestions of the National Bureau of Standards (NBS) and of Thiel, Schulz and Coch (TSC). Potentiometric measurements were carried out using the PC Laboratory Multi-Parameter System LM 2000 (Sensortechnik Meinsberg GmbH, Waldheim, Germany) to evaluate the electrochemical behavior depending on the pH value.

III. RESULTS

A. Micro-X-ray fluorescence analysis (µ-RFA)

The results of µ-RFA demonstrate that the pH glass targets used for PLD possess a good homogeneity (see Figure 10).

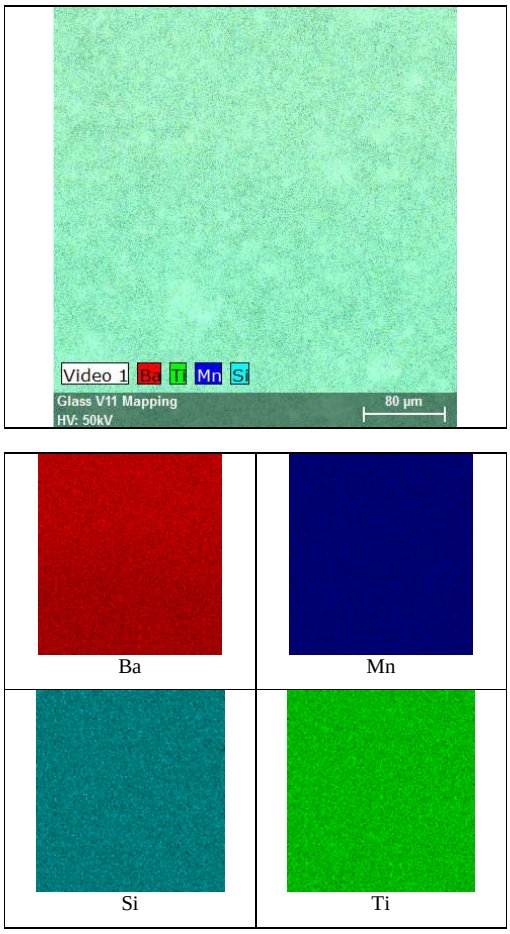

Figure 10. Element mapping of a PLD-based pH glass thin film

Element mappings exhibit a uniform distribution of the elements over the entire analyzed surface; no pronounced defects or areas with an accumulation of an element were detected. This ensures - compared to conventional glass electrodes made by a glassblower - identical conditions of the sensor membrane concerning the interface between measuring solution and electrode surface.

Subject of the investigations was the layering structure of the new pH thin film sensor according to Figure 11, consisting of a substrate (laboratory glass or alumina) with a sputtered gold basic electrode and a sensitive pH glass layer deposited by PLD. Finally, an isolation epoxy layer was applied.

Figure 11: pH thin film electrode

Consequently, the possible presence of gold on the sensor surface will be an indicator for a defect in the PLD based pH glass thin film.

B. *Scanning electron microscopy (SEM)*

Figures 12 and 13 show SEM images of two different pH glass membranes, which were deposited by PLD process on glass substrates with a sputtered gold basic electrode on it.

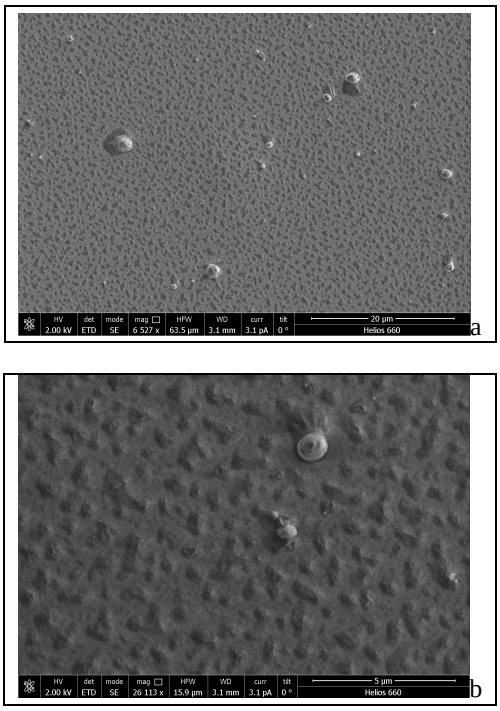

Figure 12. SEM images of Li-pH glass membrane manufactured by PLD Magnification. 6527x (a) and 26113x (b)

As it is to be seen, there are no holes and cracks and only a few droplets on the surface of the thin film.

Small anomalies are to be found specifically in Figure 15 for a Li-containing pH glass. The results of up to date XRD measurements - not presented in this article - suggest that there are no crystallites or areas of segregation.

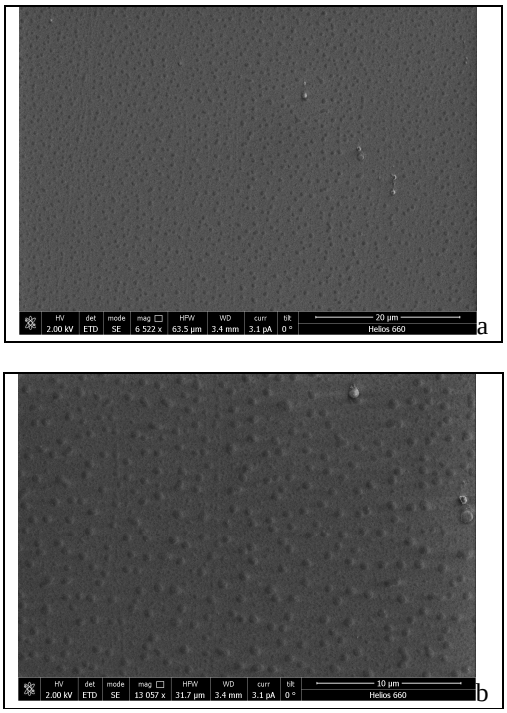

Figure 13. SEM images of a high-temperature pH glass membrane manufactured by PLD - Magnification. 6522x (a) and 13057x (b)

C. *X-ray photoelectron spectroscopy (XPS)*

Both - the used glass targets and the fabricated PLD based pH glass thin films - were investigated by means of XPS.

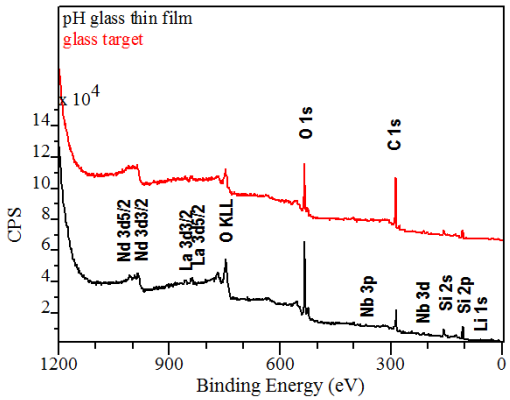

Figure 14. Comparative presentation of XPS spectra from a glass target and a pH glass thin film obtained from this target by PLD

Overview spectra and spectra of the single elements in regions of their highest sensitivity were recorded.

In an exemplary manner, Figure 14 demonstrates a comparative presentation of the overview spectrum from a glass target and of a glass thin film deposited from this source by PLD. These spectra showed no differences in the chemical composition. In addition, a determination of the gold content on the surface of the pH thin film sensors was carried out (see Figure 15). There are no peaks at the typical positions for binding energies of gold to be found in the spectra that would indicate a presence of gold on the surface. This suggests that there are no holes in the thin pH sensitive glass and that this layer is tight.

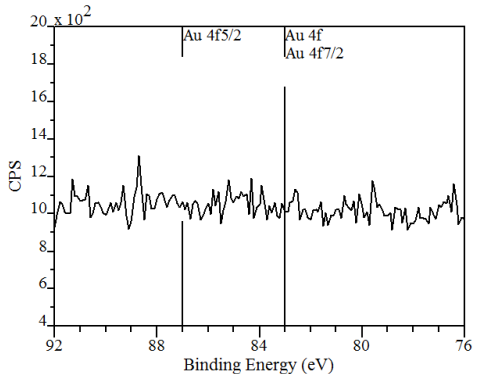

Figure 15. XPS spectrum recorded on a PLD based glass thin film, region of the highest sensitivity for gold

D. XRD

The recording of diffractograms by means of two-dimensional X-Ray diffraction (XRD)[2] is an appropriate tool for the characterization of glass based thin films. Using a High-Resolution Diffractometer with a general area detection diffraction system (GADDS), the detection limit of crystalline amounts can be reduced into a sub-percentage range. The X-Ray diffraction patterns of the PLD films in Figure 16 show significant first sharp diffraction peak, even in sub-µm thicknesses.

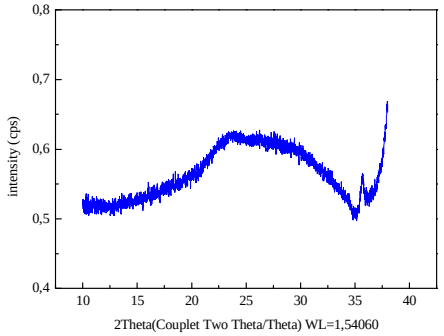

Figure 16. Diffractogram of pH glass thin film

E. Electrochemical Characterization

The investigations concerning the electrochemical behavior were carried out in NBS and TSC pH-buffer solutions at 25 °C [23].

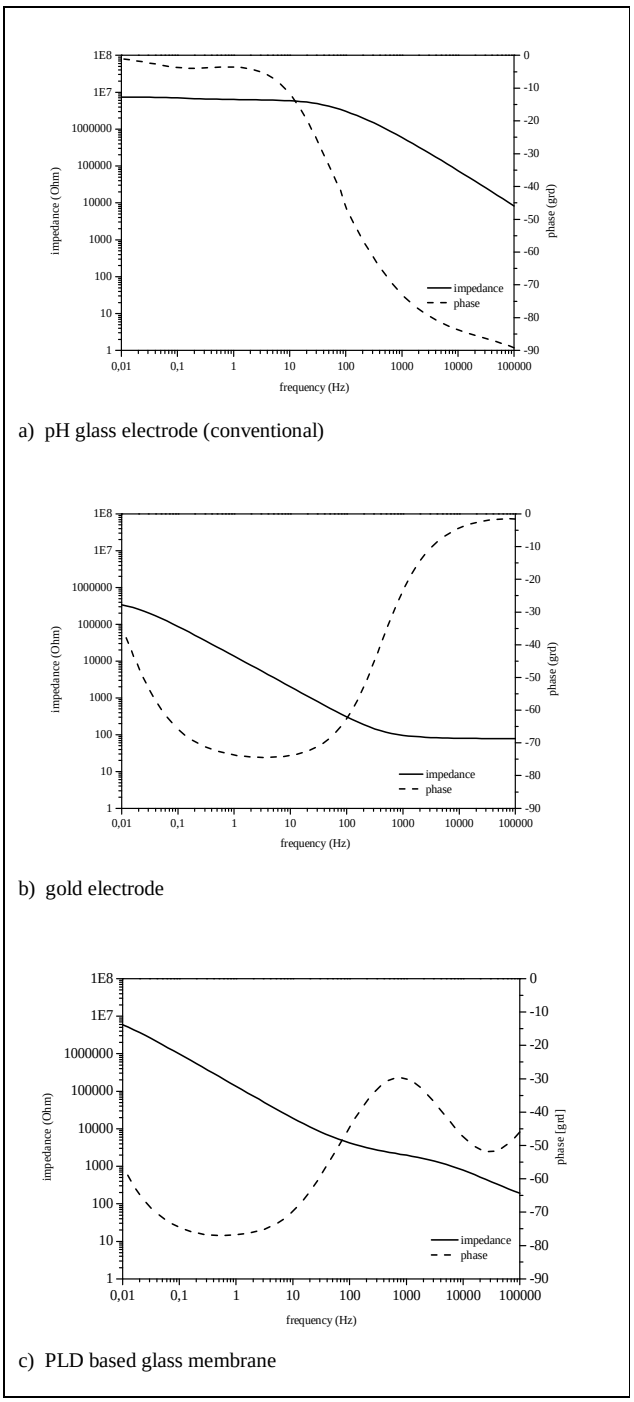

Figure 17. Impedance spectra in a NBS-buffer solution (pH=6.86)

EIS measurements

For EIS measurements in NBS-buffer pH=6.86 (Figure 17) a three electrode arrangement was used, consisting of a working electrode (a traditional glass electrode, a PLD glass membrane electrode with the same glass composition or a gold basic electrode), a KCl-saturated silver chloride reference electrode and a platinum sheet as counter electrode.

The resulting Bode-Plots in the diagrams look quite different. As expected, the impedance of the traditional glass electrode (Figure 17a) is significantly higher than that of the gold electrode (Figure 17b) due to the high glass resistance.

The impedance of the PLD glass membrane is lower than that of the conventional glass electrode – because of the lower thickness – but even higher than that of the gold electrode. This gives an indication, that the PLD glass membrane was deposited tightly and without holes. Nevertheless, the phase characteristic in Figure 15c is not fully understood yet.

pH measurement

Previous studies, as already mentioned above, were mainly carried out to adapt PLD technology for coating planar metallized glass substrates with ion conducting selective glass films. Only a few electrodes were tested for pH-measurements until now.

Figure 18 shows the pH dependence of one of the first PLD electrodes in TSC buffer solutions, measured at 25 °C versus an Ag/AgCl//$KCl_{sat.}$-electrode as a reference electrode.

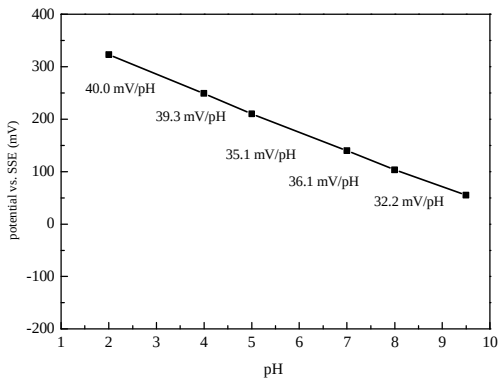

Figure 18. Potential measurement with thin-film pH glass electrode in TSC-buffer solutions

Actually, the PLD glass electrodes do not demonstrate the electrochemical sensitivity of the conventional glass electrodes filled with electrolytic solutions. Here, it could already be shown that PLD based pH glass layers in direct metal contact deliver sensor sensitivities of approximately -32 mV/pH to 40 mV/pH at 25 °C.

Currently, it is not ensured that a stoichiometric deposition of the functional pH glass takes place in the PLD process. Results of element determination in the deposited thin films by inductively coupled plasma optical emission spectrometry (ICP-OES) and flame photometry suggest that there are losses especially in the case of the alkaline content. If this will be confirmed by further investigations, an adjustment of the glass compositions is absolutely necessary, because changes in the glass composition cause a reduction of pH sensitivity.

Drift behavior and long-term stability have to be optimized for the reasons outlined above by forthcoming integration of interlayers. In case of a positive outcome of the development with respect to resolution, repeatability and accuracy, a realization of miniaturized planar all solid state glass electrodes with properties comparable to at the moment widely used sensor types can be expected. Electrodes with layers prepared by PLD technology should deliver measurement signals with a higher repeatability. This is due to the fact that this manufacturing process provides a better reproducibility of the thicknesses of the deposits.

For the fabrication of corresponding pH glass electrodes with constant stable electrode potentials and electrode functions following the Nernst equation the realization of an additional semi- or mixed conducting interlayer (for example zinc oxide [13]) by the same technology is necessary [24]. This will be the subject of future projects.

IV. CONCLUSIONS AND OUTLOOK

In the present contribution, PLD technology is introduced as a new method for the deposition of sensitive glass membranes with high variability in the choice of the glass composition. Analyzing results and first electrochemical applications of the glass thin film electrodes are described.

Homogeneity and leak-tightness of thin glass films fabricated in such way could be demonstrated by µ-RFA and XPS analyses. Due to the low thickness of the glass membrane planar PLD based pH sensors possess clearly smaller electrode resistances compared to those obtained by glass blowing and screen printing. This fact, as well as the possibility to deposit the sensitive membranes on different sensor substrate materials (glass, ceramics) offer a variety of applications, e.g., in the area of cell research. Here and in a lot of biomedical and biotechnological applications, the transparency of glass is an important progress.

It should be also mentioned that the previously established thin film method for the fabrication of chemo sensors (CHEMFETs) is mainly based on CMOS technology. This requires high investment and running costs and can be introduced economically only if products with

identical composition and design are needed in large quantities. The described sensor fabrication by means of PLD allows, amongst others, to abstain completely from using photolithographic processes and additional encapsulation steps with simultaneous cost-efficiency also for small and medium quantities. The sensors described in this contribution work according to the potentiometric principle contrary to CHEMFETs. Thus, future appliers can still use their measurement devices for conventional sensors.

Furthermore, in the future it should be possible to fabricate glass based multi sensors by means of the described method. This could be the case for planar probes to determine other monovalent cations than H^+. For this purpose, it will be necessary to place several targets in the vacuum chamber and to vary the deposition conditions. Under such circumstances, it will be also possible to realize potentiometric multi sensors with several selective membranes consisting not only of glasses. Realizable seems a combination of electrode glasses with defined metal oxide layers with analytical electrode function in solutions, such as vanadium oxide [25, 26].

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