PLD as Possible Tool for the Fabrication of Chemosensors Based on Amorphous Membranes

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Abstract— **Electrochemical sensors with sensitive membranes from amorphous materials, in particular, in case of pH electrodes are traditionally fabricated by glass-blowers. For a more effective manufacturing, sometimes so-called blowing machines are used. Thereby, on the one hand a miniaturisation of these electrodes is limited due to technological reasons. On the other hand, this makes it impossible to achieve planar sensors. In addition, a relatively large amount of functional special glass is necessary for such processes. Pulsed laser deposition (PLD) could provide ideal conditions to reduce the above-mentioned drawbacks. In this contribution results of using this method for the fabrication of planar glass based electrochemical sensors are demonstrated, whereby an amorphous silicate glass is in the focus for the sensor membrane.**

Keywords- ***electrochemical sensor; pulsed laser deposition; planarity; sensor miniaturisation; thin film.***

I INTRODUCTION

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

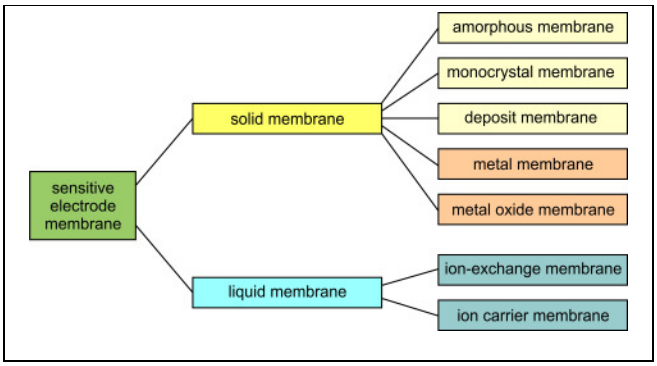

Figure 1. Classification of membrane materials for electrochemical sensors

For solid membranes, amorphous materials play a significant role. 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 [1]. The membrane materials used here are silicated glasses with high electrolytic conductivity which mainly are achieved by using alkaline, as well as alkaline earth metal oxides, changing the silicate glass network [2] like is shown in Figure 2.

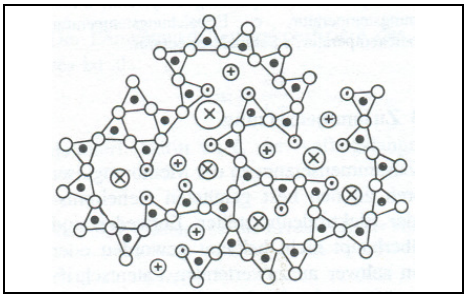

Figure 2. Two-dimensional structure of a silicate glass with network changing components
● Si, o brige oxygen bridge, Θ separate oxygen, ⊗ network changing component, ⊕ cation

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 and subsequent quenching. 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 in its interiors containing a buffer solution and an electrochemical reference system (as a rule an electrode of 2nd kind). Modifying the glass composition makes it possible to realise 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 [3].

Beside the above mentioned sensors, whose functionality is based on electrolytic conductivity, there are also probes with electron conducting amorphous membrane materials. These include redox glass [4] and chalcogenide glass electrodes [5]. 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. Liquid system components therefore are not applicable for chemosensors based on such materials. From constructional view on the one hand it is possible to fabricate compact electrodes by

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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).

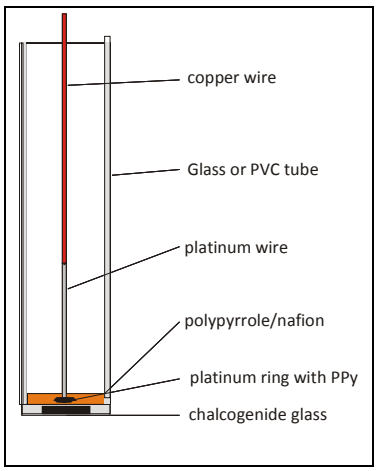

Figure 3. Schematic drawing of a chalcogenide glass electrode [6]

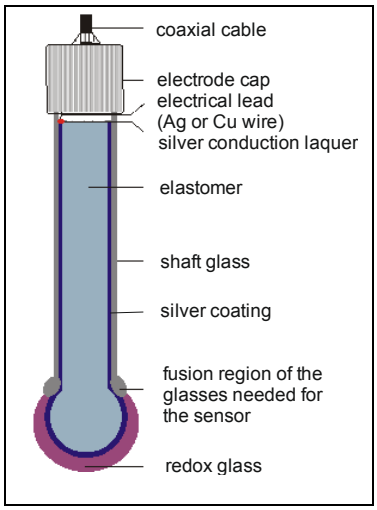

Figure 4. Schematic drawing of a redox glass electrode [7]

Also for silicate glass based cation selective electrodes, due to the purpose of their application, it is an interesting task to replace the common liquid system components by solids. The functionality causing electrolytic conductivity of siliceous pH- but also pLi-, pNa or pK-glasses [8] 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 (for example a metal) leads to a so called blocked interface and consequently to an unfavourable measurement behaviour [9].

In the past, several suggestions were made to realise 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 [10]. Previous work on corresponding all solid state glass electrodes dealed with sensors fabricated with precision manufacturing techniques and screen printing (see Figure 5a+b). Here, a clear stabilisation of the half cell potentials over the time could be obtained compared to a direct metal contacting [11].

Following, it is reported on investigations using PLD as fabrication technology to realise planar all solid state pH electrodes according to above described approach, in other words to the forming of a layer design metal/ mixed conducting interlayer / cation selective amorphous membrane on dielectric substrates (SiO_2, oxide ceramic, glass).

Beside the realisation of an adherent metallic basic electrode and a semiconducting metal oxide film special attention will be paid to the transfer of the functional sensor layer from a prefabricated ion selective target material by the laser to the substrate. In this process, on the one hand, no material losses may occur. On the other hand, also the target component must be amorphous. This paper is focused on the results of research work focused on this fundamental subtask to create all solid state pH glass layers in PLD.

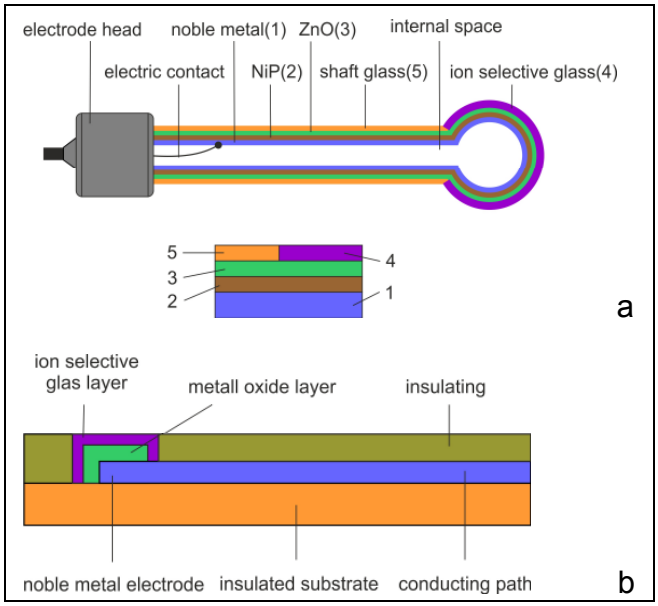

Figure 5. All solid state pH glass electrodes based on ZnO as interlayer
a fabricated in fine and glass mechanics according to [12]
b fabricated in thick film technology according to [13]

In section II, the fabrication of the glass targets, the PLD process for the glass layer deposition and the characterisation of these layers are described. Results of micro-X-ray fluorescence analysis, X-ray photoelectron spectroscopy and electrochemical impedance spectroscopy are presented in section III.

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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 mould according to Figure 6. This manufacturing method delivers homogeneous and also amorphous target materials with defined geometries. According to Figure 7 glass cylinders were fabricated that were singularised in discs with a thickness of 5 mm by means of a precision saw (Accutom-50, Fa. Struers).

Figure 6. Pouring of molten glass in a graphite mould

Figure 7. Targets of pH glass

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“ of the company Creavac (see Figure 8) was used which provides both deposition processes. Furthermore, a simultaneous substrate and mask handling is possible without an interruption of the vacuum during the coating process.

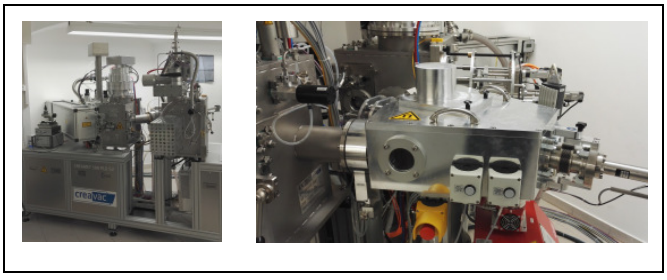

Figure 8. Combined coating system CREAMET 500 PLD S2 of the company Fa. Creavac, sputter chamber
left: mask and substrate handler and PLD chamber
right: mask und substrate handler with transfer device

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 x 10^{-2} mbar under an argon atmosphere. As chamber pressure for the following sputtering processes of the adhesive layer (Ti) and the electrical conducting discharge electrode (Au) a value of 7.0 x 10^{-3} mbar was used. 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 in the PLD coating chamber using a carrier and the PLD process was started. The deposition of the thin pH glass films was conducted by a KrF excimer laser source (ComPexPro 110 of the company Coherent) 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 x 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 club (On-Axis-PLD).

C. Characterisation

The thin films of pH sensitive glasses prepared by PLD were comprehensively characterised with respect to material composition and electrochemical behaviour. A possibility for the nondestructive determination of homogeneity and material composition of thin pH glass films is micro-X-ray fluorescence analysis. The energy dispersive micro-X-ray fluorescence system M4 Tornado (Fa. Bruker Nano GmbH, Berlin) was used for the position-sensitive elemental analysis and allows the analysis of large and inhomogeneous samples as well as smallest particles fast and at low vacuum under environmental conditions.

With X-ray photoelectron spectroscopic measurements the chemical composition in the first few atomic layers of a material surface can be detected because of a low excitation energy of only 12.5 kV compared to values of other radiographically methods like, e.g., µ-RFA with excitation energies up to 50 kV.

The new pH thin film sensors presented here use gold as discharge material for the electrochemical potential formed at the sensor surface in contact with the analyte. This interlayer between glass substrate and pH sensitive glass layer was deposited by laser ablation. Thus, the existence of gold on the sensor surface is an indicator for the tightness of the PLD-based pH glass thin film. To demonstrate this tightness the measurement system SAGE HR 100 Compact High

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Resolution (company SPECS Surface Nano Analyses GmbH) was used. The excitation of the sample was carried out with $Mg_{K\alpha}$-radiation and an X-ray power of 250 W. To evaluate the electrochemical behaviour, in particular for the estimation of the electrical conductivity of the glass thin films, impedance measurements were carried out in a neutral NBS buffer solution (pH= 6.86) by means of the potentiostat Gamry Interface 1000 (company Gamry Instruments Inc.).

In addition to the here described micro-X-ray fluorescence analysis and X-ray photoelectron spectroscopy, which allows 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 and x-ray diffraction as further radiographical research methods. Their application shows that it is possible to realise amorphous sensor membranes using PLD as thin film production method.

III RESULTS

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

The results of µ-RFA demonstrate that PLD coated pH sensitive glass films possess a good homogeneity (see Figure 9).

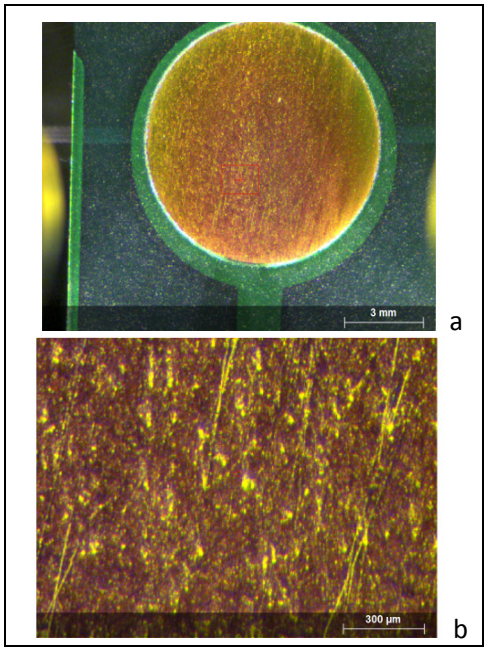

Figure 9. PLD-based pH glass thin film on glass substrate with Au/Ti-conducting path 10x magnification (a) and 100x magnification (b)

Element mappings deliver a uniform distribution of the elements over the entire analysed surface; no pronounced defects or areas with an accumulation of an element were detected (see Figure 10). This ensures compared to conventional glass electrodes identical conditions of the sensor membrane concerning the interface between measuring solution/ surface.

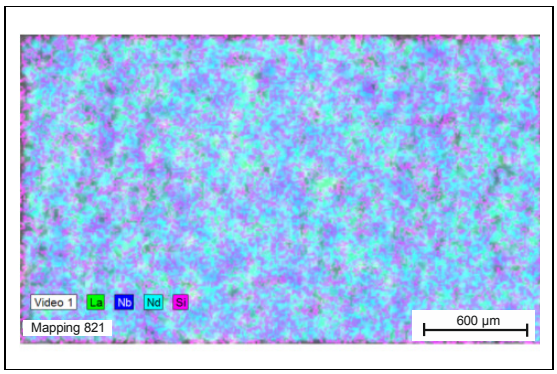

Figure 10. Element mapping of a PLD-based pH glass thin film

B. *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 overview spectra and spectra of the single elements in regions of their highest sensitivity. Figure 11 demonstrates in an exemplary manner a comparing 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 12).

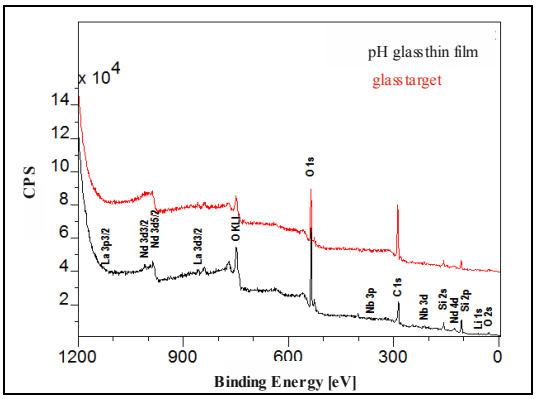

Figure 11. Comparing presentation of XPS spectra from a glass target and a pH glass thin film obtained from this target by PLD

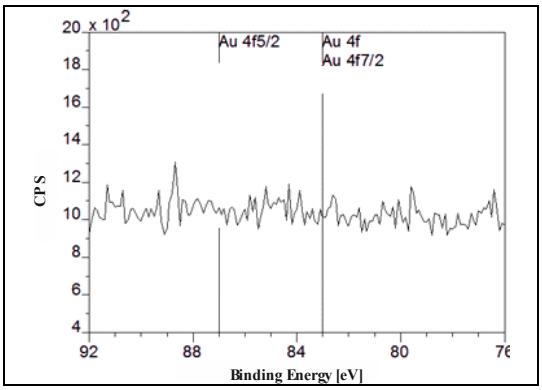

Figure 12. XPS spectrum obtained at a PLD based glass thin film, region of the highest sensitivity for gold

The spectra indicate that there are no holes in the pH sensitive layer and that this layer is tight because no peaks at the typical positions for binding energies of gold and its compounds are present.

C. Electrochemical Impedance Spectroscopy (EIS)

Figure 13 shows results of EIS determinations using a pH glass thin film and a glass bead as working electrode, in each case a KCl-saturated silver chloride electrode as reference and a platinum sheet as counter electrode. Although the phase characteristic in Figure 13a is not yet understood advantageously, a clearly lower electrode resistance can be identified for the PLD based electrode (Figure 13b). By the way, electrodes with layers produced by PLD technology 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.

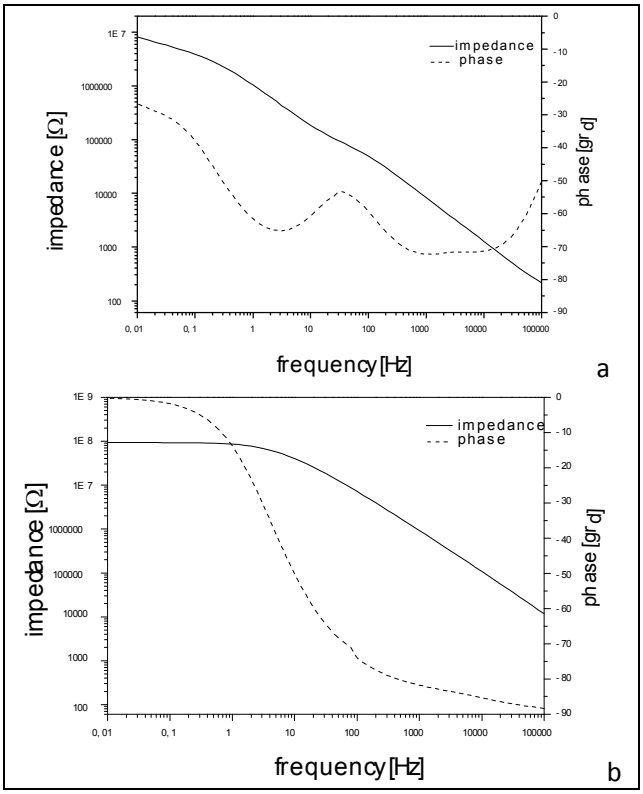

Figure 13. Impedance spectra of the 3-electrode system: thin film glass (a) and glass bead (b)/Ag/AgCl, KCl_{sat}/ Pt in a NBS-buffer solution (pH=6.86)

D. pH measurement

Previous studies, as already written above, in the main were carried out to coat planar metallised glass substrates with ion conducting selective glass films by improving and adapting PLD technology for this special purpose. For the fabrication of corresponding pH glass electrodes with constant stable electrode potentials and electrode functions following the Nernst equation the realisation of an additional semi- or mixed conducting interlayer (for example zinc oxide [12]) by the same technology is necessary [14]. This will be the subject of future projects.

However, it could already be shown, that PLD based pH glass layers in direct metal contact deliver sensor sensitivities of approximately -42 mV/pH at 25 °C. Drift behaviour and long-term stability have to be optimised 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, it can be expected to realise miniaturised planar all solid state glass electrodes with properties comparable to widely used sensor types.

IV CONCLUSIONS

In the present contribution, results derived from the application of PLD as a new method for the deposition of sensitive electrode glasses 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 significantly smaller electrode resistances compared to conventionally fabricated ones. This fact, as well as the possibility to deposit the sensitive membranes on different sensor substrate materials (metal, ceramics) and also on glass offer a variety of applications, e.g. in the area of cell research. Here and in a lot of biomedical and biotechnological utilisations the transparency of glass is a strong advantage.

It should also be mentioned that the previously established thin film method for the fabrication of chemosensors (CHEMFETs) is based on CMOS technology, mainly. This requires high investment and running costs and can be introduced economically only if products in large quantitites are needed. The described sensor fabrication by means of PLD allows, among others, to abstain completely from using photolithographic processes and additional encapsulation steps with simultaneous cost-efficiency also for small and medium quantities. Contrary to CHEMFETs, the sensors described in this contribution work according the potentiometric prinicple. Thus, future appliers can still use their measurement devices for conventional sensors.

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