Sensors **2004**, *4,* 156-162

sensors

ISSN 1424-8220
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Inorganic Thin-film Sensor Membranes with PLD-prepared Chalcogenide Glasses: C*hallenges and Implementation*

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Received: 01 August 2004 / Accepted: 06 September 2004 / Published: 30 October 2004

Abstract: Chalcogenide glasses offer an excellent "challenge" for their use and implementation in sensor arrays due to their good sensor-specific advantages in comparison to their crystalline counterparts. This paper will give an introduction on the preparation of chalcogenide glasses in the thin-film state. First, single microsensors have been prepared with the methods of semiconductor technology. In a next step, three microsensors are implemented onto one single silicon substrate to an "one chip" sensor array. Different ion-selective chalcogenide glass membranes ($PbSAgIAs_2S_3$, $CdSAgIAs_2S_3$, CuAgAsSeTe and TlAgAsIS) were prepared by means of the pulsed laser deposition (PLD) process. The different sensor membranes and structures have been physically characterized by means of Rutherford backscattering spectrometry, scanning electron microscopy and video microscopy. The electrochemical behavior has been investigated by potentiometric measurements.

Keywords: heavy metal detection, thin-film sensor array, chalcogenide glass material, microfabrication technique, pulsed laser deposition, potentiometry.

Introduction

Intensive investigations in the field of ion-selective electrodes on the basis of chalcogenide glass materials have been carried out during the last two decades. Different chalcogenide glasses for the detection of heavy metals in aqueous media were presented. The advantages of chalcogenide glass-based sensors are the high chemical stability of these vitreous materials in comparison to their crystalline counterpart, their good long-term stability and the low detection limit [1-4].

For modern and miniaturized sensor devices, however, it is necessary to prepare the sensitive material in a fast and cost-effective way. This especially becomes very interesting in terms of multi-sensor systems for the simultaneous measurement of different ions in solutions. One approach, therefore, is the use of well-established methods of semiconductor technology. The deposition of chalcogenide glasses by means of such conventional techniques is, however, somewhat problematic and not sufficiently realized so far.

Recently, a new technology for the deposition of chalcogenide glass materials as thin films onto a given silicon substrate could be introduced, namely the pulsed laser deposition technique. This technique became its "breakthrough" in the end of the eighties. Due to the discovery of high-temperature superconductors, the PLD represents an important tool for the preparation of a wide spectrum of functional materials, like e.g. diamond-like carbon [5]. Another field for PLD is the fabrication of optical wave guides with low optical losses and the realization of complex oxides for the fabrication of high-temperature superconducting quantum interference detectors [6]. The advantage of the PLD is the stoichiometric transfer of even complex materials, e.g. chalcogenide glasses, to be deposited into their thin-film state, an easy set-up and short process times [5-8]. Different chalcogenide glass systems ($PbSAgIAs_2S_3$, $CdSAgIAs_2S_3$, CuAgAsSeTe and TlAgAsIS) have been prepared as thin-film sensors for the detection of heavy metals (Pb^{2+}, Cd^{2+}, Cu^{2+} and Tl^{+}) in aqueous media [9-12].

The integration of different chalcogenide glass-based thin films onto one sensor chip offers the possibility to realize multi-sensor systems. As a first step, three different chalcogenide glass materials for the detection of Pb^{2+}-, Cd^{2+}- and Cu^{2+}-ions in aqueous solution have been integrated onto one silicon chip. The thin films have been physically characterized by means of Rutherford backscattering spectrometry, scanning electron microscopy and video microscopy [7-13]. The electrochemical sensor characterization has been performed by means of ion-selective potentiometry and impedance spectroscopy. In this paper, latest results will be presented and discussed.

Experimental

Two different sensor structures have been fabricated by means of semiconductor technology. On the one hand, single microsensor structures and on the other hand, sensor arrays have been realized.

For the fabrication of the single microsensors, a p-doped (Bor) 3" single-crystal silicon wafer (Wacker-Chemitronic) with <100>-orientation, specific resistance of >1000 Ωcm and thickness of 381±25 µm has been used. As a first fabrication step, a 300 nm SiO_2 layer was grown up onto the silicon substrate by means of thermal wet-oxidation (oxidation oven, Tempress). To realize the contacts for the microsensors, it is necessary to structurize the wafer by means of photolithography.

The photolithographical process is subdivided into three different steps: 1.) Spin-coating of a positive photoresist (AZ 5214, Hoechst) onto the silicon substrate. To improve the adhesion between the photoresist and the silicon wafer, hexamethyldisiloxan was used. 2.) To define the structure of the microsensor, the photoresist was exposured through a mask via a mask aligner (MA 6, Suss-microtech), which consists the structure of the microsensors. 3.) Finally, the photoresist was developed through a chemical developer (AZ 312 MIF, Clariant). The contacts of the microsensors were prepared by means of electron-beam evaporation (PLS 500, Balzers). A contact layer system of Ti:Pt:Au with a thickness of 30:175:300 nm was deposited. As a last step to remove the areas with photoresist, a lift-off process with acetone and isopropanol was done. After these steps, the whole wafer was cut into single chips with a length of 20 mm*10 mm. The fabrication process of the sensor arrays is described in detail in [13].

For the deposition of the different chalcogenide glass membranes, the "off-axis" PLD process was applied. The PLD device consists of a KrF-excimer laser (LPX 300, Lambda) with a wavelength of 248 nm, and a repetition rate of 10 s^{-1} with a energy density of 5 Jcm^{-2}. The PLD process was accomplished in a vacuum chamber with N_2 atmosphere to prevent any oxidation of the deposited material at a pressure of $2*10^{-1}$ mbar and room temperature. The laser beam is focused on the rotating target material with the different "conventional" chalcogenide glass materials ($PbSAgIAs_2S_3$, $CdSAgIAs_2S_3$, CuAgAsSeTe and TlAgAsIS). The principle of the off-axis PLD process is shown in Figure 1.

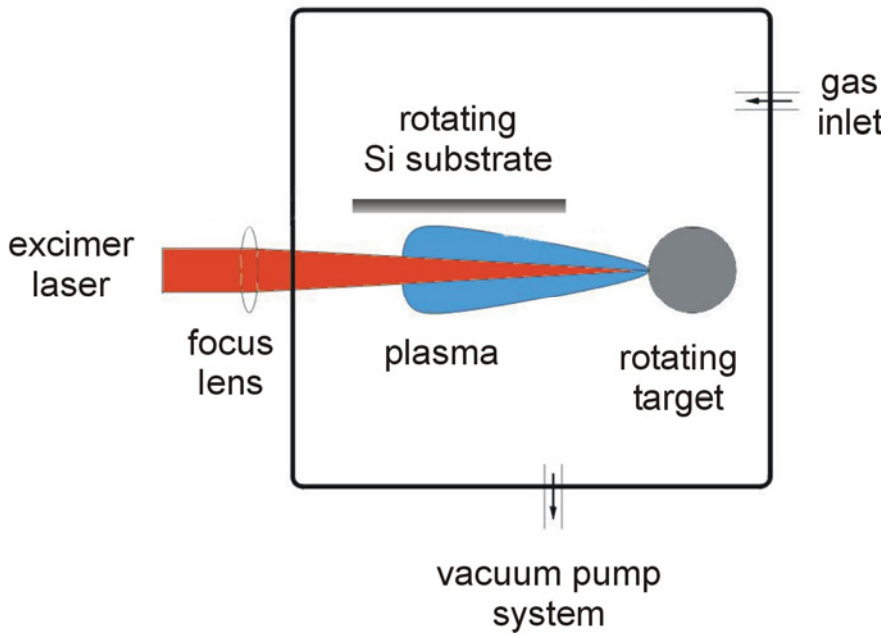

Figure 1. Principle of the off-axis pulsed laser deposition process.

The description of the interaction of the high-energy laser beam with the target material can be explained in four distinct steps: 1.) Absorption of the laser beam 2.) Melting of the target surface 3.) Vaporization of the target material. 4.) Plasma emission. These four steps are carried out during a laser pulse of about 30 ns.

In case of the sensor arrays, the PLD process was performed through a Al mask with an open hole for the respective chalcogenide glass thin film. After the PLD process, the single microsensors and the sensor arrays have been glued on a printed circuit board (PCB), wire-bonded and encapsulated by an epoxy resin (EPO-TEK 87-GT, Polytec).

To study the electrochemical behavior of the single microsensors and sensor arrays, they were measured in the respective solution towards a conventional Ag/AgCl double-liquid junction reference electrode (inner solution: 0.1 mol/l KCl, outer solution: 0.1 mol/l KNO_3). The measurement data are recorded by means of a multi-meter system with a high input impedance (Type 2700, Keithley) and a multiplier system (Type 7700, Keithley) to measure simultaneously up to 20 channels in the differential mode. To control the measurement system, a conventional personal computer was connected via a general purpose interface bus. For the single microsensors, the potentiometric response has been characterized in Pb^{2+}-, Cd^{2+}-, Cu^{2+} and Tl^{+}-solutions in terms of sensitivity, stability, pH range and detection limit. The concentration range of the solutions was from 10^{-7} mol/l up to 10^{-2} mol/l. The determination of the selectivity coefficient (K_{sel}) has been determined by means of the fixed interference method in solutions of Zn^{2+}-, Ni^{2+}-, Co^{2+}-, Fe^{2+}-, Ca^{2+}-, Mg^{2+}-ions. The influence of the pH value on the sensor response was studied in solutions with constant ionic strength and a constant heavy metal concentration. The sensor arrays have been characterized in Pb^{2+}-, Cd^{2+}-, and Cu^{2+}-solutions in terms of sensitivity and stability. The concentration range of the solutions was from 10^{-6} mol/l up to 10^{-2} mol/l. For a constant ionic background, 0.1 mol/l KNO_3 solution was used for all measurements. All used chemicals are from reagent grade.

Results and discussion

For the single microsensors, a video microscopic picture is exemplarily shown in Figure 2 (a). After the PLD process, the single sensor chip as well as the sensor array (see Figure 2 (b)) were glued on a PCB board, contacted to the conducting track for the electrical connection of the respective chalcogenide glass thin films and encapsulated with an epoxy resin. The diameter of the sensing surface is about 5 mm and 2 mm for the single sensors and the sensor arrays, respectively. For the electrical connection, ultrasonic wedge bonding was used.

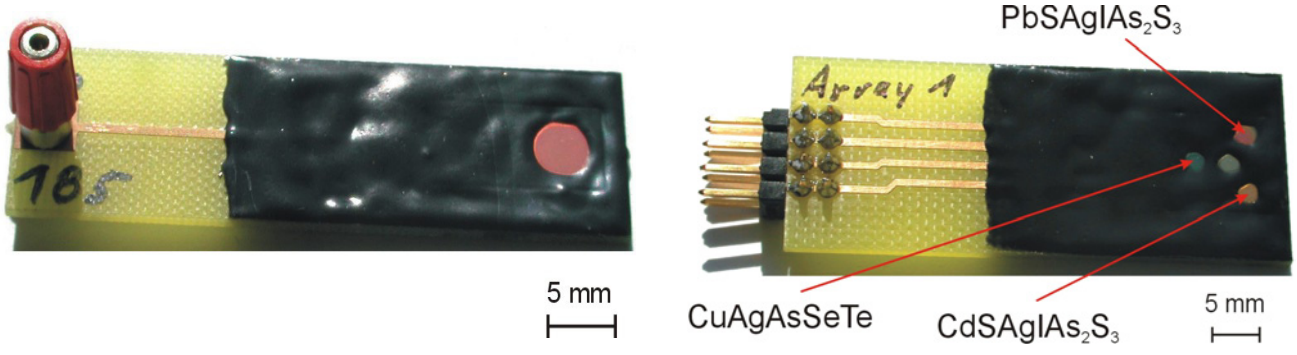

Figure 2. (a) Video-microscopic picture of a lead thin-film single microsensor ($PbSAgIAs_2S_3$) and (b) of the thin-film sensor array with three different chalcogenide glass thin films.

The electrochemical behavior of the single microsensors and the sensor arrays was investigated by means of ion-selective potentiometry. A nearly-Nernstian response over 6 concentration decades was observed for the different chalcogenide glass microsensors. In case of the lead microsensor, the sensitivity was about 26-29 mV/pPb, the cadmium and copper microsensors show a sensitivity of 25-28 mV/pCd and 27-30 mV/pCu, respectively. For the univalent ion (thallium), the sensitivity was about 54-60 mV/pTl. The detection limit of the microsensors was about $1x10^{-7}$ mol/l (lead), $4x10^{-7}$ mol/l (cadmium), $1x10^{-7}$ mol/l (copper) and $3x10^{-5}$ mol/l (thallium). The electrochemical parameters of the chalcogenide glass microsensors are summarized in detail in Table 1.

Table 1. Electrochemical parameters of the chalcogenide glass microsensors.

Material:	PbS-AgI-As_2S_3	CdS-AgI-As_2S_3	Cu-Ag-As-Se-Te	Tl-Ag-As-I-S
Ion:	Pb^{2+}	Cd^{2+}	Cu^{2+}	Tl^{+}
Sensitivity:	26-29 mV/pPb	25-28 mV/pCd	27-30 mV/pCu	54-60 mV/pTl
Selectivity: (K_{sel}) *	$Cd^{2+} \rightarrow 0.05$ $Zn^{2+} \rightarrow 2x10^{-5}$ $Ni^{2+} \rightarrow 1x10^{-5}$ $Co^{2+} \rightarrow 2x10^{-5}$ $Fe^{2+} \rightarrow 1x10^{-4}$ $Ca^{2+} \rightarrow 5x10^{-5}$	$Pb^{2+} \rightarrow 33$ $Zn^{2+} \rightarrow 2x10^{-4}$ $Ni^{2+} \rightarrow 1x10^{-3}$ $Co^{2+} \rightarrow 1x10^{-3}$ $Fe^{2+} \rightarrow 2x10^{-3}$ $Ca^{2+} \rightarrow 3x10^{-3}$	$Pb^{2+} \rightarrow 5x10^{-5}$ $Cd^{2+} \rightarrow 4x10^{-5}$ $Zn^{2+} \rightarrow 3x10^{-6}$ $Ni^{2+} \rightarrow 6x10^{-6}$ $Co^{2+} \rightarrow 5x10^{-6}$ $Ca^{2+} \rightarrow 1x10^{-5}$	$Pb^{2+} \rightarrow 1x10^{-2}$ $Cd^{2+} \rightarrow 1x10^{-2}$ $Cu^{2+} \rightarrow 0.5$ $Zn^{2+} \rightarrow 5x10^{-4}$ $Ca^{2+} \rightarrow 2x10^{-5}$ $Mg^{2+} \rightarrow 2x10^{-5}$
Stability:	> 250 d **	> 230 d **	> 230 d **	> 160 d **
pH range:	2-7	2.5-8	2-6	2-5
Detection limit:	$1x10^{-7}$ mol/l	$4x10^{-7}$ mol/l	$1x10^{-7}$ mol/l	$3x10^{-5}$ mol/l

* determined by fixed interference method, ** current data

The results for the sensor arrays are comparable to that of the single microsensors and the conventional chalcogenide glass bulk-electrodes in terms of sensitivity and selectivity [14]. The sensitivity of the different chalcogenide glass thin films (lead, cadmium and copper) showed also a nearly-Nernstian behaviour in sensitivity and a long-term stability of at least 30 days (current data).

Conclusions

The challenge and implementation of PLD-prepared chalcogenide glass thin films have been presented. Single microsensors and sensor arrays have been fabricated by means of silicon technology. Different ion-selective chalcogenide glass membranes have been deposited by means of the off-axis PLD process. Is has been demonstrated that it is possible to miniaturize the conventional chalcogenide glass electrodes due to their transfer in the thin-film state. The electrochemical behavior of the chalcogenide glass thin films has been studied by means of ion-selective potentiometry. The measurements were done in Cd^{2+}-, Pb^{2+}-, Cu^{2+}- and Tl^{+}-solutions in the concentration range from

10^{-7} mol/l to 10^{-2} mol/l. The sensitivity, stability, detection limit and pH range were investigated. The fixed interference method was used to determine the selectivity coefficients towards different ions. Moreover, three chalcogenide glass thin films were implemented to one common silicon substrate to a "one-chip" sensor array. The electrochemical behaviour of the sensor array is comparable to that of conventional bulk electrodes and single microsensors. Due to the presented results it is possible to combine several different chalcogenide glass thin films onto one given substrate. This combination enables the design of a thin-film sensor-based analysis system. The arrangement of such a sensor array might be a first step towards a miniaturized "electronic tongue" set-up [14-16]. While the development of several thin-film sensors on one single sensor chip has been already successfully demonstrated in this work, additional software implementation (e.g., fuzzy logic, artificial neural network) is necessary to finally end up in the realization of a *p*ortable *e*lectrochemical *t*est system for *r*eal-time *a*nalysis (PETRA) for environmental analysis.

Acknowledgements

The authors gratefully thank D.-T. Knobbe, A. Steffen, J. Müller, A. Pracht and R. Stockmann for valuable discussions, and the Ministerium für Wissenschaft und Forschung des Landes Nordrhein-Westfalen for financial support.

References

1. Vlasov, Yu.G.; Bychkov, E.A. Ion-selective chalcogenide glass electrodes. *Ion-selective Electrode Rev.* **1987**, *9*, 5.
2. Vlasov, Yu.G. New solid-state ion-selective electrodes – Sensors for chemical analysis of solution. *Fres. Z. Anal. Chem.* **1989**, *335*, 92.
3. Vlasov, Yu.G.; Bychkov, E.A.; Legin, A.V. Chalcogenide glass chemical sensors: research and analytical applications. *Talanta* **1994**, *41*, 1059.
4. Legin, A.V.; Bychkov, E.A.; Vlasov, Yu.G. Analytical applications of chalcogenide glass chemical sensors in environmental monitoring and process control. *Sen. Actuators B* **1995**, *24-25*, 309.
5. Chrisey, D.B.; Hubler, G.K. *Pulsed laser deposition of thin films.* John Wiley & Sons, INC.: New York, Toronto, **1994**, pp. 1-113.
6. Saenger, K.L. Pulsed laser deposition part I a review of process characteristics and capabilities. *Proc. of Adv. Mat.* **1993**, *3*, 1.
7. Schöning, M.J.; Mourzina, Yu.G.; Schubert, J.; Zander, W.; Legin, A.; Vlasov, Yu.G.; Lüth, H. Can pulsed laser deposition serve as an advanced technique in fabricating chemical sensors? *Sens. Actuators B* **2001**, *78*, 273.

8. Schöning, M.J.; Schubert, J.; Kloock, J.P.; Zander, W.; Mourzina, Y.G.; Legin, A.; Vlasov, Y.G.; Lüth, H. Innovative thin film techniques for microfabricating electrochemical sensors. *Biocybernetics Biomed. Eng.* **2001**, *21*, 107.

9. Schubert, J.; Schöning, M.J.; Schmidt, C.; Siegert, M.; Mesters, St.; Zander, W.; Kordos, P.; Lüth, H.; Legin, A.; Mourzina, Yu.G.; Seleznev, B.; Vlasov, Yu.G. Chalcogenide-based thin film sensors prepared by pulsed laser deposition technique. *Appl. Phy. A* **1999**, *69*, 803.

10. Mourzina, Yu.; Schöning, M.J.; Schubert, J.; Zander, W.; Legin, A.; Vlasov, Yu.G.; Kordos, P.; Lüth, H. A new thin-film Pb microsensor based on chalcogenide glasses. *Sens. Actuators B* **2000**, *71*, 13.

11. Mourzina, Yu.G.; Schöning, M.J.; Schubert, J.; Zander, W.; Legin, A.V.; Vlasov, Yu.G.; Lüth, H. Copper, cadmium and thallium thin film sensors based on chalcogenide glasses. *Anal. Chim. Acta* **2001**, *433*, 103.

12. Schöning, M.J.; Mourzina, Yu.G.; Schubert, J.; Zander, W.; Legin, A.; Vlasov, Yu.G.; Lüth, H. Pulsed laser deposition – An innovative technique for preparing inorganic thin films. *Electroanalysis* **2001**, *13*, 727.

13. Kloock, J.P.; Mourzina, Yu.G.; Schubert, J.; Schöning, M.J. A first step towards a microfabricated thin-film sensor array on the basis of chalcogenide glass materials. *Sensors* **2002**, *2*, 356.

14. Vlasov, Yu.G.; Legin, A.; Rudnitskaya, A. Cross-sensitivity evaluation of chemical sensors for electronic tongue: determination of heavy metal ions. *Sens. Actuators B* **1997**, *44*, 532.

15. Ahlers, H. *Multisensorpraxis*, Springer-Verlag: Berlin, Heidelberg; New York, **1996**, pp. 182-365.

16. Vlasov, Yu.; Legin, A.; Rudnitskaya, A. Electronic tongues and their analytical application. *Anal. Bioanal. Chem*. **2002**, *373*, 136.

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