HEAVY METAL DETECTION WITH SEMICONDUCTOR DEVICES BASED ON PLD-PREPARED CHALCOGENIDE GLASS THIN FILMS

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1. Introduction

Chalcogenide glass materials as membranes for potentiometric sensors for chemical analysis in solutions have been extensively studied in the past. Ion-selective electrodes with chalcogenide glass membranes dealt with the ion-sensing properties of this class of materials, followed by systematic investigations of their solid-state chemistry, the sensing mechanism and their analytical characteristics [1]. Recently, the analytical performance of chalcogenide glass membranes has been combined with techniques originally invented for semiconductor processing, in order to create a new generation of silicon-based sensors with chalcogenide glass thin films for heavy metal detection. For these 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. Based on conventional chalcogenide glass bulk electrode materials, the authors have introduced the pulsed-laser deposition (PLD) process for the fabrication of complex chalcogenide glass materials in the thin-film state [2-11]. Miniaturized ion-selective electrodes (µISE), sensor array structures and field-effect structures such as the electrolyte-insulator-semiconductor (EIS) sensor, the light-addressable potentiometric sensor (LAPS) and the ion-sensitive field-effect transistor (ISFET) are selected as transducer materials for the readout of the sensor signal. The results for different chalcogenide glass materials together with different transducer structures will be presented.

2. Experimental and results

The different transducer structures (µISE, sensor array, EIS, LAPS and ISFET) have been fabricated by means of silicon planar technology. For the fabrication of the different sensor membranes, the pulsed-laser deposition process has been utilized (for experimental details, see [2-11]). The main advantage of the PLD process is the stoichiometric transfer of even complex

materials – as in the case of chalcogenide glass materials – that can be deposited into their thin-film state. Moreover, the PLD process implies a relatively simple set-up and only short process times are required (when compared to sputtering or e-beam evaporation). For depositing the thin-film materials, targets of the chalcogenide glass bulk material have been chosen, consisting of $PbSAgIAs_2S_3$, $CdSAgIAs_2S_3$, CuAgAsSeTe, CuAgAsSe, TlAgAsIS and AgAsS, respectively. Therewith, the detection of typical heavy metal ions in aqueous solution, like Pb^{2+}, Cd^{2+}, Cu^{2+}, Tl^{+} and Ag^{+}, is possible. In Fig. 1, the schematic of the PLD process and the applied target materials (top), and the different transducer structures (bottom) are shown.

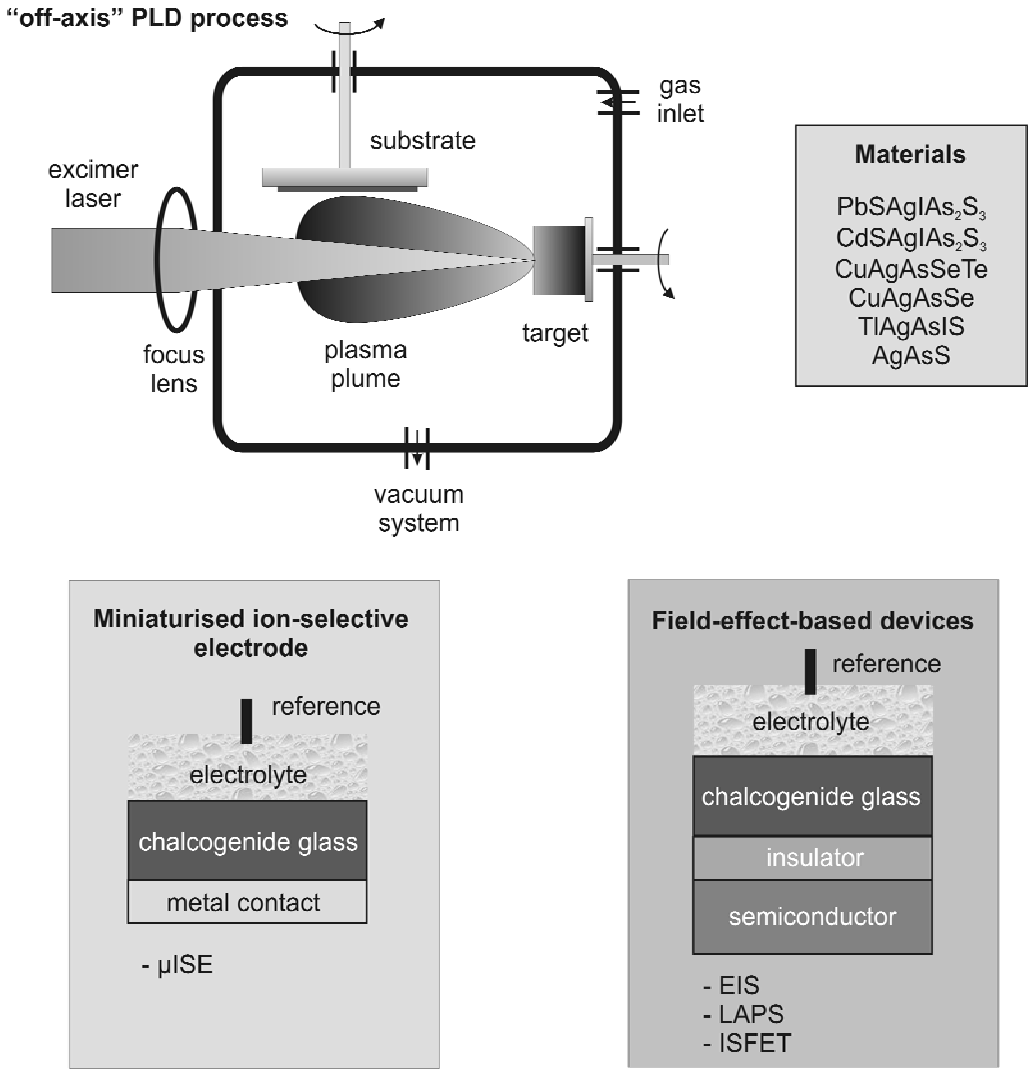

Fig. 1. Schematic of the PLD process (top) and different transducer structures of the sensors utilized in this work (bottom).

In order to validate the stoichiometric transfer from the original target to the thin-film state and to study the morphology of the deposited layers, Rutherford backscattering spectrometry and scanning- and transmission electron microscopy have been performed. For the electrochemical

sensor characterization, ion-selective potentiometry (μISE), capacitance/voltage and constant capacitance measurements (EIS), current/voltage and constant current measurements (LAPS), and constant charge mode (ISFET) measurements were used. The results of the electrochemical sensor characterization of the fabricated semiconductor devices based on PLD-prepared chalcogenide glass thin films are summarized in Table 1.

Table 1. Summary of the electrochemical parameters of the fabricated field-effect- and μISE thin-film sensor structures [2-11]

Ion (X) to be determined	Chalcogenide glass material	Sensitivity (mV/pX)	Detection limit (mol/l)	Selectivity: Ksel*	pH range	Stability (days)
Pb^{2+}	Pb-S-Ag-I-As-S	26-29	$1x10^{-7}$	Ag^{+}, Hg^{2+}→ interference, Cd(II)→0.05, Zn(II)→$2*10^{-5}$, Ni(II)→$1*10^{-5}$, Co(II)→$2*10^{-5}$, Fe(II)→$1*10^{-4}$, Fe3+→~0.8, Ca(II)→$5*10^{-5}$	2-7	250
Cd^{2+}	Cd-S-Ag-I-As-S	26-28	$4x10^{-7}$	Ag^{+}, Hg^{2+}, Cu^{2+}→interference, Pb(II)→33, Zn(II)→$2*10^{-4}$, Ni(II)→$1*10^{-3}$, Co(II)→$1*10^{-3}$, Fe(II)→$2*10^{-3}$, Fe3+→~10, Ca(II)→$3*10^{-3}$	2.5-8	>230
Cu^{2+}	Cu-Ag-As-Se-Te	27-30	$1x10^{-7}$	Ag^{+}, Hg^{2+}→interference, Pb(II)→$5*10^{-5}$,Cd(II)→$4*10^{-5}$, Zn(II)→$3*10^{-6}$, Ni(II)→$6*10^{-6}$, Co(II)$5*10^{-6}$, Fe3+→~0.6, Ca(II)→$1*10^{-5}$	2-6	230
Tl^{+}	Tl-Ag-As-I-S	54-60	$3x10^{-5}$	Cu(II)→0.5, Zn(II)→$5*10^{-4}$, Pb(II), Cd(II), H+→$1*10^{-2}$, Ca(II), Mg(II)→$2*10^{-5}$	2-5	160
Cu^{2+}	Cu-Ag-As-Se	27-29	$1x10^{-7}$	Ag^{+}, Hg^{2+}→interference, Pb(II)→$5*10^{-5}$,Cd(II)→$2*10^{-5}$, Zn(II)→$2*10^{-6}$, Ni(II)→$8*10^{-6}$, Co(II)→$3*10^{-6}$, Ca(II)→$7*10^{-6}$	-	-
Ag^{+}	Ag-As-S	56-60	$<10^{-6}$	-	-	-

*determined by fixed interference method

3. Conclusions

The present work might serve as a basis for future handheld “electronic tongue” systems based on chalcogenide glasses. The experiments could demonstrate that the thin-film preparation

of chalcogenide glass materials can be realized on silicon-based μISEs, sensor arrays and different field-effect structures (EIS, LAPS, ISFET). In future work, additional ion-selective membranes can be combined together with pattern recognition algorithms to an intelligent sensor array for heavy metal monitoring in liquid test samples.

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