Transport in nanostructured porous silicon layers

A. Kovacs, U. Mescheder

Institute for Applied Research, Furtwangen University, Robert-Gerwig-Platz 1, 78120 Furtwangen, Germany

Abstract

Transport mechanisms such as diffusion, adsorption, desorption and capillary condensation of gases or fluidics in porous materials play an important role when using these materials for sensing or filtration. Transport processes were investigated in freestanding porous silicon (PS) membranes for liquids and gases. Additionally, transport of liquids (organic and aqueous solutions) and vapors was characterized in PS optical multilayers used for optical sensing. Response time for adsorption processes is in the range of s. Desorption time depends on the vapor pressure of the investigated adsorbates. Adsorption and desorption isotherms are measured to investigate interactions between sample surface and adsorbate and to evaluate specific surface area and pore size distribution of porous material.

© 2011 Published by Elsevier Ltd. Open access under CC BY-NC-ND license.

Keywords: porous silicon; nanofiltration, diffusion; permeability; optical multilayers; capillary condensation

1. Introduction

Porous silicon (PS) can be widely used as material e.g. for sensing [1,2] or filtration. Here, transport of gaseous or liquid media will determine the characteristics of according devices. Also in the fabrication process of PS (anodization in HF with ethanol) transport mechanisms through the already formed PS are important [3]. Investigation of transport processes in nanostructured silicon layers provides important information for successful application of porous materials in MEMS and NEMS.

2. Experimental and results

2.1. Fabrication of freestanding porous silicon membranes

Freestanding PS membranes for nanofiltration applications (Fig.1) have been fabricated with membrane areas from 1mm² to 2,25mm², thicknesses from 10μm to 20μm, pore size radius typically in the micro- and mesoporous range (with mean pore size radius from 1,5nm to 3nm), and with porosity
from 70% to 80%. The permeable porous membranes were characterized both, for gas and fluidic filtration in dead-end and cross-flow filtration mode, respectively (Fig. 2). Bursting pressures of such membranes are measured up to 0.6 bar.

Fig. 1. Schematic (a) and scanning electron microscope (b) picture of the investigated free standing porous silicon membrane.

Fig. 2. Measurement setups for permeability measurements of liquid (a) and gas (b) transports in PS membranes.

2.2. Permeability measurements of porous silicon membranes

PS membrane modules are permeable for both, gases and liquids (Fig. 3a and 3b). The permeability for liquids was approved by an aqueous NaCl solution. The NaCl concentration can be changed by about 6 orders of magnitude by wetting the feed side with the NaCl-solution. Typical flow rates of 0.1 l/h-0.3 l/h for nitrogen was found (Fig. 3b), depending on the transmembrane pressure. Gas transport (flow rate) in direction of the electrochemical etching in PS layers is 13% larger than in the opposite direction.

Fig. 3. (a) NaCl concentration on the feed and permeate side of the investigated PS membrane using periodical permeate side wetting by variation of the transmembrane pressure (TMP). (b) N2 flow rate in the function of the transmembrane pressure (TMP) through a 20 μm thick PS membrane with membrane area of 1 mm² and mean pore size radius of 2.1 nm.

2.3. Fabrication of porous silicon based optical multilayers

Transport of different organic and aqueous solutions has been characterized also in porous silicon based optical multilayers (Fig. 4). PS based optical multilayer stacks have been realized using periodical variation of refractive index in low doped silicon substrate.
2.4. Adsorption and desorption processes in porous optical multilayers

In such layers the loading, saturation, adsorption and desorption time of e.g. methanol, ethanol and toluol can be characterized by the optical measurement of the spectral shift of the peak position of the so-called stop-band [2]. Adsorption takes place in 1-3 sec for the investigated liquids and in 5-7 sec for the investigated vapors. Desorption times show a strong dependence on the partial vapor pressure of the according organic liquid (Table 1).

Table 1. Time responses of the stop-band peak position shifts in desorption phase using methanol, ethanol and toluol.

| Analyte   | Desorption time in native PS | Vapor saturation Pressure [hPa] |
|-----------|-------------------------------|---------------------------------|
| Methanol  | 45                            | 129                             |
| Ethanol   | 63                            | 58                              |
| Toluol    | 180                           | 29                              |

For an exact transport model the different limitations of adsorption and desorption phase and the according different critical pore parameters have to be considered. Adsorption and desorption isotherms have been measured (Fig. 5a) and corresponding pore size distributions evaluated using BJH theory (Fig. 5b). Time response of desorption process is determined by the smallest pore size which is generated at low current density in case of multilayer stacks. The pore size is taken from the desorption branch of the measured isotherm. The evaluated mean pore size in adsorption and desorption phase shows a difference of 0,29nm (Fig. 5b). The bottle neck effect leads to deceleration of the desorption process. Aqueous solutions have more than 20min natural desorption time due to the higher interactions between sample surface and adsorbate.

Fig. 5. (a) N2 Adsorption-desorption isotherms for native PS layer anodized in 30w.t. %HF with 20mA/cm² current density and 10-15Ωcm Si-substrate. (b) Derived pore size distribution in the adsorption and desorption phase for native PS layers using 0-15Ωcm Si-substrate, anodized in 30w.t.% HF using 20mA/cm² current density.
3. Discussion and conclusion

Different transport mechanism are known in porous silicon layers, such as molecular or gaseous flow, Knudsen flow, surface diffusion, multilayer diffusion, capillary condensation and configurational diffusion. Transport processes are depending on the layer morphology (pore size, porosity, tortuosity), surface treatment, surface interactions between adsorbate and substrate, adsorbate properties and vapor pressure of the investigated adsorbates [4]. Diffusion mechanisms depend on the relation between pore diameter and mean free path of the sorbate molecules (Fig 6). The mean free path in the investigated porous membrane is larger than the pore diameter therefore Knudsen diffusion is expected however surface adsorption have to be taken into account [5]. Capillary condensation occurs in pores of PS based optical multilayers whose radius is smaller than the Kelvin radius. Response times for adsorption processes in PS based multilayer using liquids are in the range of 1-3 sec and using vapors in the 5-7 sec range. Natural desorption depends on the vapor pressure of the investigated adsorbates. Additionally, desorption process shows a strong dependence on surface treatment and adsorbate properties. The difference of gas flow rate in direction of the pore formation and in the opposite direction is attributed to the specific pore shape caused by the electrochemical pore etching process.

![Diffusion models in the function of the pore size (a) and schematic picture of combined diffusion model (b).](image)

Fig. 6. Diffusion models in the function of the pore size (a) and schematic picture of combined diffusion model (b).

Acknowledgements

The authors would like to thank for the financial support of the Baden-Wuerttemberg Stiftung for the project “Micro- and nanotechnology based Filter systems”.

References

[1] P. Fürjes, A. Kovács, Cs. Dúcso, M. Ádám, B. Müller and U. Mescheder. Porous Silicon Based Humidity Sensor with Interdigital Electrodes and Internal Heaters. *Sensors and Actuators* B 95, 2003, 188-193

[2] A. Kovacs, P. Jonnalagadda and U. Mescheder. Optoelectrical detection system using porous silicon based optical multilayers. *IEEE Sensors Journal*, 2011, accepted for publication

[3] Alexey Ivanov, Andras Kovacs, Ulrich Mescheder. High quality 3D shapes by silicon anodization. *Phys. Status Solidi A* 208, No. 6, 1383–1388 (2011) / DOI 10.1002/pssa.201000163

[4] R.M.A Roque-Mallerbe. *Adsorption and diffusion in nanoporous materials*. CRC Press, Taylor & Francis Group, Boca Raton, FL, 2007.

[5] D. M. Ruthven, W. J. DeSisto, S. Higgins. Diffusion in a mesoporous silica membrane: Validity of the Knudsen diffusion model. *Chemical Engineering Science* 64 (2009) 3201-3203