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Silicon-based microreactors as research tools in chemistry

ABSTRACT

In this contribution suitability of silicon-technology based microreactors for performing research on reactions where temperature control is essential is discussed. The versatility of silicon micromachining technology is elucidated by describing the fabrication and performance of two types of microreactors for studying Rh-catalyzed gas phase reactions. Depending on the design of the microreactor, working temperatures up to 800 °C can be obtained.

INTRODUCTION

Microdevices like microreactors have fundamental advantages in comparison with conventional macroscale systems due to their characteristic dimensions in the sub-micrometer to the sub-millimeter range (1, 2). These dimensions result in small internal volumes and high surface-to-volume ratios, which lead to improved heat and mass transfer rates. As a consequence, fast reaction control is possible while only small amounts of chemicals are needed (2-4), which makes microreactors extremely suitable for performing and studying in a safe way reactions under extreme conditions of temperature and pressure or reactions involving flammable or toxic species. The high thermal conductivity of silicon and the possibility of Very Large Scale Integration (VLSI) of control functionality like temperature sensors, heating filaments and flow sensors, make silicon-based microreactors useful research tools for investigations on reactions where temperature control is essential (1, 2, 5-7). This paper will discuss the fabrication and characterization of silicon microreactors designed for the study of high temperature rhodium-catalyzed oxidation reactions.

MICROREACTOR WITH INTEGRATED HEATERS AND SENSORS ON AN ULTRATHIN SILICON MEMBRANE

A silicon-based microreactor was developed on the basis of published layouts (5 ,7), which contains a flow channel etched in silicon capped with an ultrathin composite membrane consisting of silicon and silicon nitride, with on the outside thin-film heaters and sensors, and on the inside a thin-film catalyst patch (Figure 1).
The thickness and composition of the membrane is important, from a thermal and mechanical point-of-view. For fast heating of the catalyst and gasmixture, this thickness should be minimized. On the other hand, fast cooling of the gasmixture in the eventual case of runaway of exothermic reactions requires also high transverse heat transport through the membrane, which would speak for a thicker membrane. In order to control high temperature reactions, the characteristic heat transfer time-constants of the microreactor have to be substantially smaller than the residence time of ca. 10 milliseconds (8). The mechanical stability of the membrane is threatened by the requirement of fast thermal response, which implies large temperature gradients which may result in buckling or rupture of the membrane (5). A compromise on the thickness and composition of the membrane was found, using a thermo-mechanical model, in a composite membrane composed of 850 nm of heavily boron-doped monocrystalline silicon and 150 nm of low-stress silicon nitride (8).

Fabrication

The fabrication of such a composite membrane with a relatively large size of 30 mm x 500 µm and a uniform thickness is the real challenge in the development of this microreactor. In short, the fabrication process is as follows (9): a 525 µm thick p-type (100)-oriented silicon wafer was doped on one side with boron to obtain a p^{++}-Si layer of 850 nm, on which 150 nm of low-stress silicon-rich silicon nitride (SiRN) was deposited. On the backside of the wafer a 500 µm deep flow channel was etched using reactive ion etching (RIE) followed by 20 minutes immersion in a 25 wt.% KOH solution at 75 °C. The flow channel was finished by etching 15 minutes in 31 wt.% KOH saturated with isopropanol at 75 °C to release the membrane of all silicon except the boron doped layer. The result of this etching procedure is a flow channel with a length of 30 mm, a depth of 525 µm and a width of 500 µm. Magnetron sputter deposition of 20 nm thick rhodium patches at the inner side of the membrane was performed via a 3D self-aligning shadow mask. A Pyrex plate with powderblasted inlets and outlets (circular throughholes with a diameter of 450 µm) was anodically bonded to the silicon wafer so that the flow channel becomes closed. Prior to dicing, thin-film heaters and temperature sensors composed of 10 nm Ta and 200 nm Pt were evaporated on the outer side of the membrane through another shadow mask. Gas connections to the inlet and outlet are realized by positioning the microreactor onto a metal plate containing tubings to mass flow controllers. These connections are ensured to be gastight by embedding Viton O-rings between the aluminum plate and the inlet/outlet and subsequent clamping of the microreactor onto this plate. Electrical connections to the heaters and sensors are made by means of a printed circuit board.

Experiments

Rh-catalyzed oxidation of hydrogen was performed as follows: after controlling the temperature of the membrane at 280 °C using the thin-film heaters, the composition of

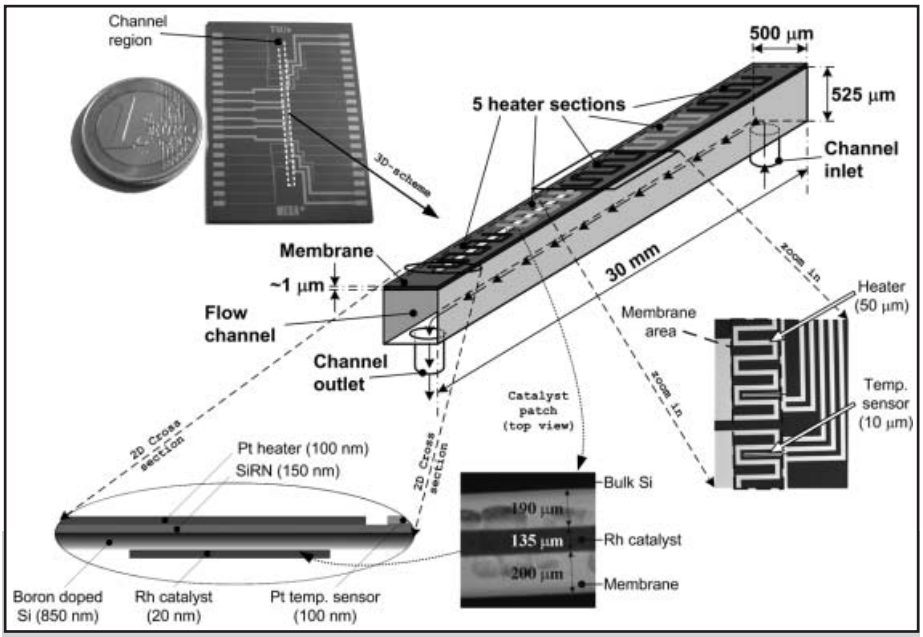

Figure 1. Picture of microreactor (3.0 x 4.5 x 0.1 cm^3) in which the flow channel region is marked. The 3D-scheme shows the heater locations on the membrane. Close-ups of the membrane with heaters and temperature sensors and the catalytic layer are shown as well as a 2D cross-sectional view of the channel, all with typical dimensions

the inlet gasmixture was changed from a non-explosive composition (44 percent H_2 – 0 percent O_2 – 56 percent He) to a stoichiometric composition of (45 percent H_2 – 23 percent O_2 – 32 percent He). During this composition change, the temperature of the membrane increased to 400 °C. Figure 2a plots the temperature of the membrane, measured with the integrated temperature sensors, as a function of the amount of converted hydrogen. In Figure 2b the gasmixtures fed to the microreactor are displayed in a reactant-space diagram, demonstrating that these microreactors are clearly capable of handling otherwise explosive gas conditions.
For temperatures up to 400 °C no mechanical problems were observed and thermal response times of ca. 1 millisecond were obtained (9). Oxidation reactions at temperatures above 450 °C, e.g. Rh-catalyzed direct partial oxidation of methane into synthesis gas, was not possible in these microreactors, due to electrical breakdown of the dielectric silicon nitride layer on the membrane. This is a design issue: it can be solved by avoiding the sandwich construction of a dielectricum confined between two conductors, viz. p^{++}-Si and platinum thin-film heaters.

MICROREACTOR WITH INTEGRATED HEATERS AND SENSORS IN SILICON NITRIDE TUBES

A way to prevent the above-mentioned electrical breakdown of the dielectric material is to omit the silicon part of the membrane. However, in order to avoid membrane rupture due to thermal stresses at temperatures above 550 °C (5), mechanical decoupling zones have to be included in the silicon nitride membrane. A microreactor was developed that contained a SiRN-membrane with integrated corrugated zones (Figure 3), making this microreactor suitable for Rh-catalyzed direct partial oxidation of methane to synthesis gas, a reaction that has an ignition temperature of ca. 600 °C.
The heater is used to heat gases and catalyst patches to temperatures above 500 °C. Due to Joule dissipation of electrical power in the thin-film heating filament, the heater and membrane expand a little. The corrugated zones are used to intercept this expansion, thereby avoiding failure of the microreactor due to thermal induced stresses.

Fabrication

The basic layout of this microreactor is identical to the thin membrane microreactor: the flow channel contains 5 heaters and 12 temperature sensors, each embedded in their own, separate suspended silicon nitride tube. Fabrication of these tubes was as follows (10): with standard lithography and RIE the pattern of heaters and temperature sensors is transferred into the topside of a silicon wafer. Subsequently, an SiO_2-layer is grown, and two plasma etching steps (directional with CHF_3 and isotropic with SF_6) are performed, followed by removal of the SiO_2 and deposition of 1 μm SiRN. The flow channel was defined on the backside and transferred into the silicon using RIE. When the channel was etched to a specific depth, i.e. 325 μm, suspended SiRN-tubes with corrugated zones result (Figure 3). After etching, the flow channel has a length of 30 mm, a width of 500 μm and a depth of 325 μm. Catalytic patches of rhodium were sputter-deposited on these tubes using a 3D shadow mask and electron beam evaporation was used to deposit a thin-film in the SiRN-tubes. Finally, a Pyrex plate with powderblasted inlets and outlets was anodically bonded to the backside of the silicon wafer to close the flow channel. Gas and electrical connections to this

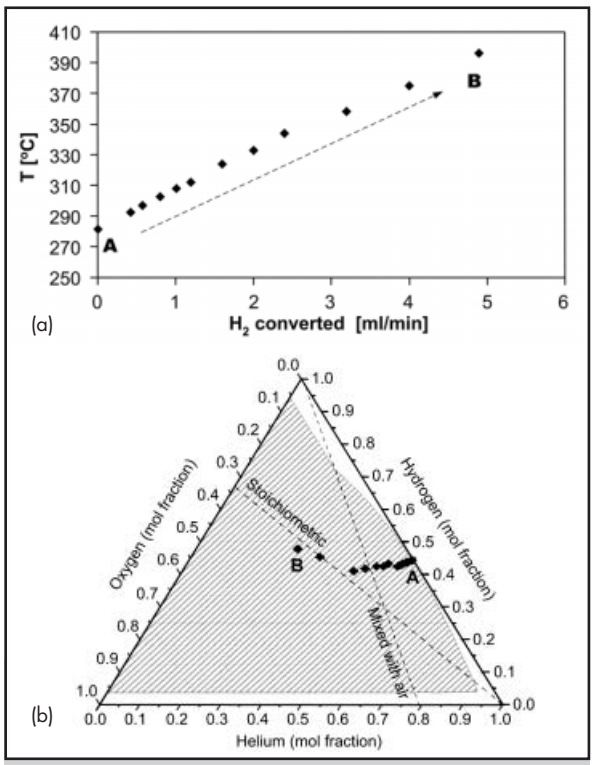

Figure 2. Temperature of membrane of microreactor during Rh-catalyzed H2-oxidation as function of the amount of converted hydrogen (a) gasmixtures provided to reactor in a reactant-space diagram (b) gray-shaded area: explosive regime)

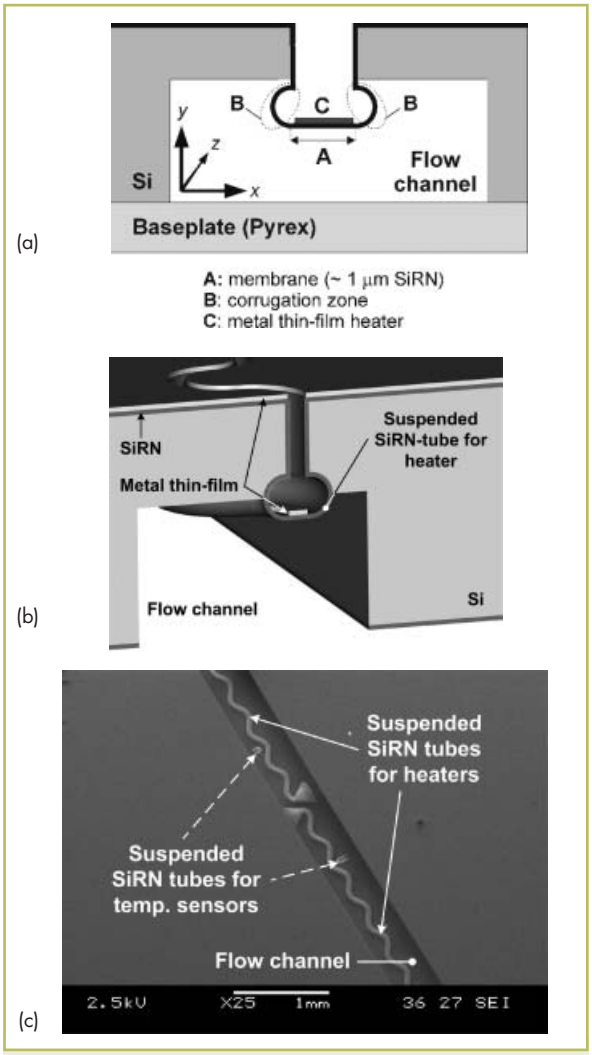

Figure 3. Schematic cross-sectional views of flow channel of microreactor that contains thin-film heaters located in SiRN-tubes that can withstand high thermally induced stresses due to inclusion of corrugated zones (a,b) - SEM-picture of suspended SiRN-tubes in the flow channel (c)

microreactor are obtained in the same way as for the thin membrane microreactor (see section 2.1).

Experiments

The high-temperature electrical behaviour of these microreactors was explored for 2 metal films, i.e. 200 nm/10 nm Pt/Ta and 200 nm Pt without adhesion layer, when exposed to a static air environment. For both films resistivity and temperature coefficient of resistance, properties that need to be well-defined for proper control of the microreactor, are subject to large fluctuations for temperatures above 500 °C. The origin of these effects are irreversible physical degradation processes that take place in thin-films when subjected to high temperatures

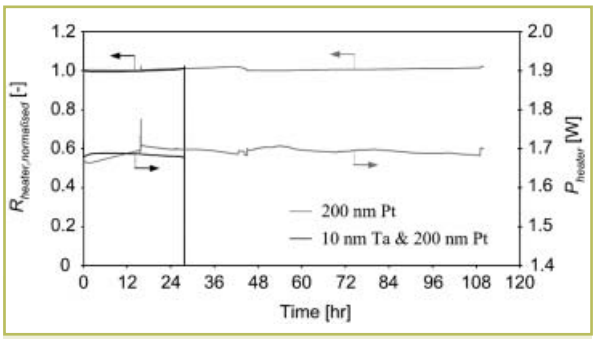

Figure 4. Normalized heater resistances ($R_{normalized,heater}$) as a function of time for thin-films of Pt/Ta and Pt thin-film during endurance experiments (Pheater ~ 1.7 W)

(11). It is noted that the degradation processes in thin-films containing Pt are much more accelerated/pronounced at high temperatures when the surrounding environments are 'reactive' (e.g. air, oxygen) instead of (relatively) inert environments (e.g. nitrogen, argon or vacuum) (11). Since these processes occur at a much slower rate in Pt thin-films than in Pt/Ta thin-films, Pt thin-films can be operated for a significantly longer time at a high temperature, and are therefore more attractive to use in microreactors. In Figure 4 the reliability of the thin-films is shown in an endurance test in which the time was determined during which the films dissipate a constant power corresponding to a heater temperature of 560 ± 50 °C. Pt/Ta films failed after 27.5h, whereas the Pt films did not fail after non-stop operation of 110h. Visual inspection showed that Pt/Ta heaters failed due to severe agglomeration of material, such that the thin-film was converted into a collection of electrically isolated islands. This effect was (almost) not visible in the Pt heaters. Additional experiments showed that microreactors with suspended SiRN-tubes containing Pt thin-films could be operated reliably and safely for more than 20h at temperatures up to 700 °C and for 10h at 800 °C. Although no Rh-catalyzed oxidation reactions are performed yet in these microreactors, it is believed that these reactors can be used as tool for research on this reaction or other high temperature reactions.

CONCLUSIONS

The fabrication and characterization of microreactors suitable for studying Rh-catalyzed gas reactions under extreme conditions of temperature is discussed. Both silicon-technology based microreactors have fast response times (~1 millisecond). The working temperature range depends on the design: thin membrane reactors can be used up to ~400 °C, whereas microreactors with embedded silicon nitride tubes can be operated up to 800 °C, showing the versatility of silicon microreactors as research tools. More general, silicon-based microreactors offer new opportunities to screen different catalytic materials in a fast and safe way: the performance (e.g. selectivity, yield and/or conversion) of catalysts can be tested as a function of feed gas composition, temperature, residence time and pressure.

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