A MICROFABRICATED SUSPENDED-TUBE CHEMICAL REACTOR FOR FUEL PROCESSING

Leonel R. Arana*, Samuel B. Schaevitz**†, Aleksander J. Franz*, Klavs F. Jensen* and Martin A. Schmidt**†
*Dept. of Chemical Engineering, **Dept. of Electrical Engineering and Computer Science
†Microsystems Technology Laboratories
Massachusetts Institute of Technology, Cambridge MA 02139

ABSTRACT

A microfabricated suspended-tube reactor has been developed and demonstrated to operate at temperatures over 900°C for efficient thermal processing of chemical fuels. This reactor uses thin-walled SiN tubes to directly address the most significant problem in small-scale fuel processors: thermal management. It efficiently isolates a high-temperature zone while maintaining a temperature gradient of up to 2000°C/mm. This design is ideally suited to serve as a combustor/recuperator for thermoelectric (TE) and thermophotovoltaic (TPV) generators, and as a reformer to produce hydrogen for portable fuel cell systems. Using the integrated heaters, catalytic ammonia cracking has been carried out to produce up to 1.6 W (9 sccm) of hydrogen with 97% fuel utilization.

INTRODUCTION

Combustible liquid fuels store up to hundreds of times more energy than state-of-the-art batteries, and are second only to nuclear fuels in the amount of energy stored per unit weight [1]. This explains why a great deal of research has focused on miniaturizing generators to convert chemical energy to electricity in low power (< 100 W) systems. Batteries still dominate, however, because generators, particularly those with moving parts and with high-temperature fuel processors, are difficult to miniaturize. Examples of such generators include fuel cell systems, in which liquid fuels are reformed into hydrogen, heat engines (e.g., TE and TPV), in which high-temperature combustion is required. Several groups have explored different approaches to high-temperature fuel processing on the small scale. Examples range from a membrane-based TE device [2] to combustion-driven mechanical engines [3]. Most efforts have focused on chemical conversions in microfluidic systems with less emphasis on thermal management and scaling. Thermal efficiency remains the key issue in these systems.

The most important requirement for a fuel processor in a power generation system, whether as burner or hydrogen generator, is that it be thermally efficient. Any heat loss to the environment is wasted energy and therefore directly undermines the efficiency of the overall process. Thermal isolation of the hot zone is very difficult in miniaturized electric generators (producing < 100 W), and even more so in MEMS generators (~ 1 W), since heat loss relative to heat generation is inversely proportional to characteristic length.

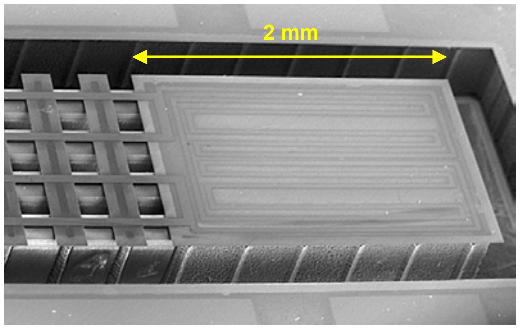

Figure 1. *SEM of F_2-released reactor showing four suspended SiN tubes connecting to the Si reaction zone, Si slabs thermally linking the four tubes, and a meandering Ti/Pt resistor*

We have developed a suspended-tube reactor/heat exchanger (Fig. 1) that is designed specifically to isolate a high-temperature zone and allow heat recuperation from process streams for efficient thermal processing of chemical fuels. The applications include on-demand hydrogen production and micro-TE and TPV generators. Our initial reaction studies have focused on ammonia cracking for hydrogen generation.

REACTOR DESIGN

The suspended-tube reactor, as shown in the schematic in Fig. 2, consists of four thin-walled (2 µm) silicon nitride tubes, comprising two separate U-shaped fluid channels.

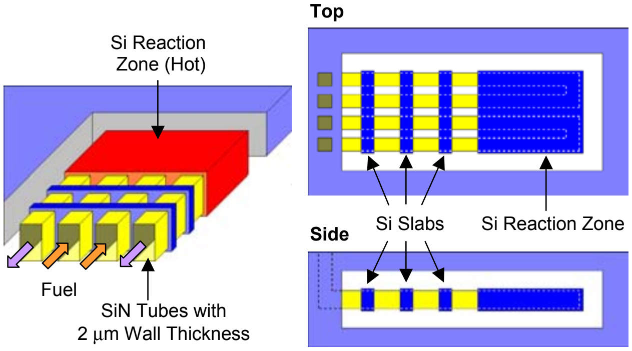

Figure 2. *Schematic of suspended-tube reactor*

On one end, the tubes are fixed into a silicon substrate containing fluidic channels and ports; on the other end, the channels are free. The free end (hot zone) is partially encased in silicon to form a thermally isolated region of high thermal conductivity in which the chemical reactions take place. The silicon nitride tubes contain silicon slabs that permit transverse heat transfer between fluid streams (for heat recuperation) without significantly adding to heat loss down the length of the tubes.

In the case of hydrogen production (e.g., ammonia cracking), combustion in one stream provides the energy required for endothermic reforming in the other stream. The high thermal conductivity of the silicon in the reaction zone facilitates heat transfer between the two process streams. In TE and TPV applications, the thermally isolated silicon zone effects a substantially isothermal fuel combustor that either heats the hot junction (TE) or radiates to a collector (TPV).

Thermal Requirements

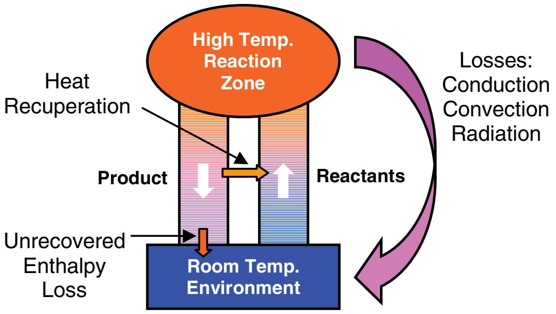

Figure 3. *Schematic highlighting the major heat loss mechanisms of a high-temperature fuel processor.*

A thermally-efficient fuel processor has two main requirements: that the hot zone be thermally isolated and that process heat (in the fluid streams) be recovered. As shown in Fig. 3, thermal isolation requires that conduction (through the solid materials and through the ambient air), natural convection, and radiation from the hot zone be minimized. Insulating materials are used in large-scale systems for this purpose. For very small cylindrical pipes (smaller than a few mm in diameter) the presence of an insulation layer actually increases the rate of heat loss to the environment [4]. Small fuel processors, therefore, unless made in complex geometries in which the fluid channels surround the hot zone on all sides, must be packaged under vacuum to eliminate conduction and natural convection through the ambient. Except in the case of TPV generation, where radiation is the useful energy form, radiation mirrors are also required to maximize thermal efficiency. In the suspended-tube reactor, heat conduction down the length of the tubes is minimized by the high aspect ratio tubes (2-µm wall thickness, 3-mm length) of silicon nitride, which is a poor thermal conductor. The second requirement, heat recuperation, is carried out by the silicon slabs cutting across at various positions along the length of the tubes.

Two-dimensional heat transfer and computational fluid dynamics models show that the thermal isolation and heat recuperation in the suspended-tube design is very effective. Fig. 4 shows a 2D temperature map of the heat recuperation for a 14-slab suspended-tube reactor. For this geometry (with 3-mm long tubes), simulations predict that between 50 and 70% of the process enthalpy can be recovered depending upon operating conditions.

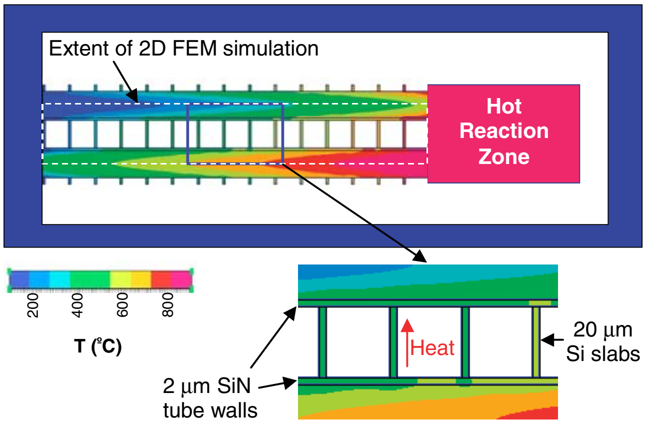

Figure 4. *Thermal behavior of two suspended, thermally-linked tubes with countercurrent fluid streams (in vacuum no radiative losses).*

Integrated Features in the Reactor

The suspended-tube reactor contains several integrated features including a thin-film heater, temperature sensors, vertical Si posts for heat transfer and catalyst support, passive liquid stop valves, and heterogeneous catalysts. A thin-film meandering platinum line serves as heater and four-point temperature sensing resistor (TSR) for the reaction zone. The leads for this heater travel along the length of the tubes on silicon nitride bridges attached to the silicon slabs. An additional TSR measure the temperature of the supporting chip. The cylindrical posts within the tubes improve the heat transfer in these regions and increase the surface area for heterogeneous chemical reaction catalysts. In addition, a passive liquid stop valve has been integrated within the reactor to localize the region in which catalyst is deposited.

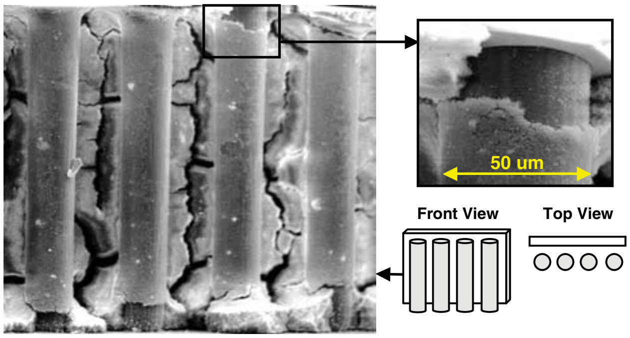

Figure 5. *SEM's of structures within the silicon reaction zone washcoated with Ir/*Al_2O_3 *catalyst.*

Unsupported and alumina-supported noble metal catalysts (as shown in Fig. 5) have been introduced into the reactor through standard washcoating techniques. This porous washcoat increases the surface area for reaction without significantly adding to the pressure drop.

FABRICATION

The tubes are made through a molding process, similar to one previously reported to make tubes for flow visualization [5], in which deep reactive ion etching and wafer bonding define the mold for subsequent deposition of low-stress nitride. We have expanded this process to include buried etched pits within the mold that allow silicon to be left surrounding the tubes in specific locations (silicon slabs and reaction zone).

1. DRIE to define fluidic ports (top) and fluidic channels and release pits (bottom)
2. Bond ultra-thin wafer on bottom side (or bond SOI wafer, thin back to oxide, remove oxide)
3. Deposit 2 μm of LPCVD low-stress nitride on all exposed surfaces
4. Pattern nitride on top and bottom to define release area
5. Deposit and pattern Ti/Pt heater/TSR on top side
6. Release structure in KOH or fluorine gas

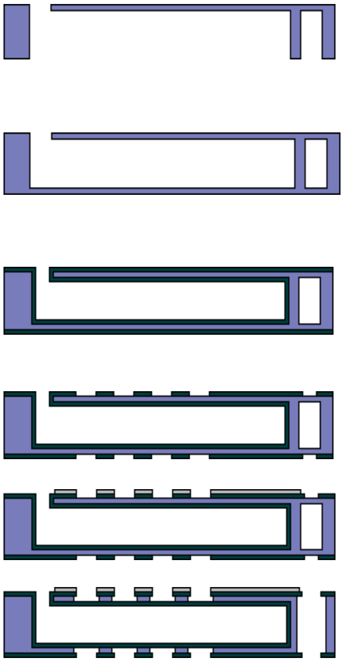

Figure 6. *Process flow for the fabrication of the suspended-tube reactor*

Fig. 6 shows the process flow for the fabrication of the suspended-tube reactor. A 100-mm double-side polished wafer is first etched (~ 40 μm) in a deep reactive ion etcher (DRIE) to define the fluidic ports. The same wafer is etched by DRIE on the back side through the majority of the wafer, until the ports from the other side are visible, to define the mold for the channels. This step also defines the release pits and structures within the reactor (posts and stop valves). The next step is to directly bond another silicon wafer to the bottom side of the first wafer. This bonded wafer can be an ultra-thin wafer (e.g., 20 μm) that is bonded directly, or an SOI wafer (with a 20-40 μm SOI layer) that is thinned back to the oxide. In either case, we are left with a wafer stack, roughly 450 μm thick with both sides sealed, except for small openings for the fluidic ports. A low-stress LPCVD silicon nitride is deposited on all exposed surfaces of the wafer stack, including the channel area inside the silicon mold and the two outer surfaces (but not inside the release pits, which are sealed). The nitride is patterned on both sides to define the release area and the location of the silicon slabs, reaction zone, and bridges for the heater leads. A thin film of Pt (with Ti adhesion layer) is deposited and patterned on the top side of the stack by electron-beam evaporation and lift-off. The last step releases the tubes from the silicon mold. We have used KOH for the release, as it is highly selective to silicon. However, KOH leaves undesirable facets on the structure and partially etches the Ti/Pt heater. For this reason we have also explored the use of fluorine gas to etch silicon.

Packaging

The packaging for the suspended-tube reactor works on two levels. The first level of packaging includes spacer chips that protect the device during handling and spread out the fluid streams on the chip to facilitate macroscopic fluidic connections. We have used low-melting-point glasses to bond these chips to the reactor chip. Ultimately, this level of packaging will also include vacuum environment necessary for efficient operation of the reactor. The next level of packaging contains the macroscopic electrical and fluidic interconnects. For laboratory testing, we have used compression sealing of an elastomeric gasket between an aluminum block containing fluidic interconnects and an acrylic plate containing electrical interconnects.

DEVICE CHARACTERIZATION

General Handling of Fluids

The suspended-tube reactor is designed to handle gases at pressures slightly above atmospheric in a vacuum package. Burst tests have shown that on average, each tube can withstand a pressure difference of 25 psi (172 kPa) across its walls. For a flow rate of 30 sccm, the pressure drop along one continuous channel is 0.07 psi (0.5 kPa) with no posts present in the reactor, and 0.40 psi (2.8 kPa) when posts are present in the reaction zone and tubes.

High-Temperature Testing

The suspended-tube reactor was heated with the integrated heaters to evaluate is thermal characteristics.

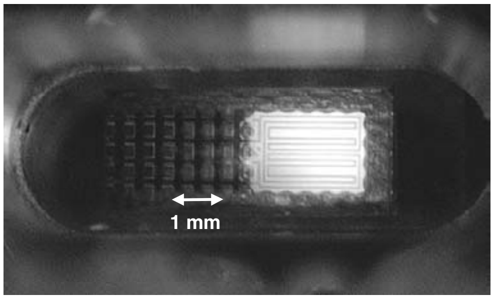

Figure 7. *Photograph of reactor heated to ~900°C in air. The supporting chip and package are below 50°C*

Fig. 7 shows a suspended tube reactor heated in air to ~900°C. This picture clearly illustrates the thermal isolation as the reaction zone glows brightly, while the tubes and supporting chips are at a much lower temperature. The U-shaped design of the silicon nitride tubes allows the structure to expand several μm from the heating while remaining structurally intact and preserving fluidic seals. We expect the reactor to be stable indefinitely at 900°C, except for the Ti/Pt heaters, which have a finite lifetime at these temperatures [6].

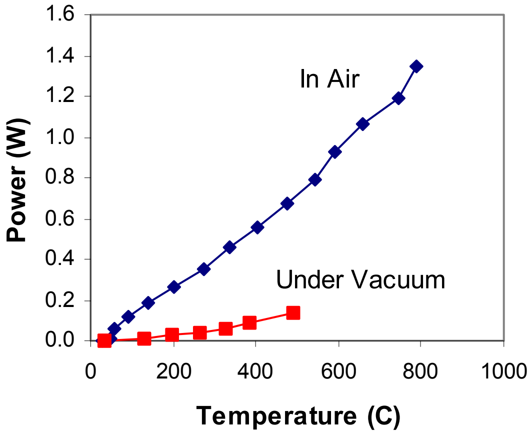

Figure 8. *Power required to heat up the reactor in air and under vacuum ambients*

As shown in Fig. 8, only ~1 W of electrical power is required to heat up the reactor to 600°C in air. In contrast, we see that ~0.2 W would be required if it were packaged under vacuum. A further breakdown of the heat loss reveals that only 0.1 W of the heater power is dissipated by conduction down the length of the tubes, while the other 0.1 W is lost by radiation. Radiative heat loss scales as the fourth-power of temperature, while conductive heat loss is linearly proportional to temperature, so we can expect that radiative heat transfer quickly dominates the conductive heat loss as the temperature exceeds 600°C. Overall, the fundamental conductive losses down the length of the tubes constitute a very small fraction of the overall heat loss, particularly at high temperatures.

AMMONIA CRACKING

We have used ammonia cracking as a model reaction to demonstrate the potential of the suspended-tube reactor to carry out efficient fuel processing reactions. Since ammonia cracking is endothermic, energy input is required for the reaction to proceed. We have performed experiments in which heat is provided by the integrated thin-film heaters to drive the cracking reaction over unsupported and alumina-supported iridium catalyst. As shown in Fig. 10, up to 1.6 W (9 sccm) of hydrogen has been produced over Ir/Al_2O_3 catalyst. This hydrogen was generated through 97% conversion of a 6 sccm feed of ammonia. This unoptimized performance translates to a generator power density of 14 kW/ℓ, compared to 100 W/ℓ for rechargeable batteries.

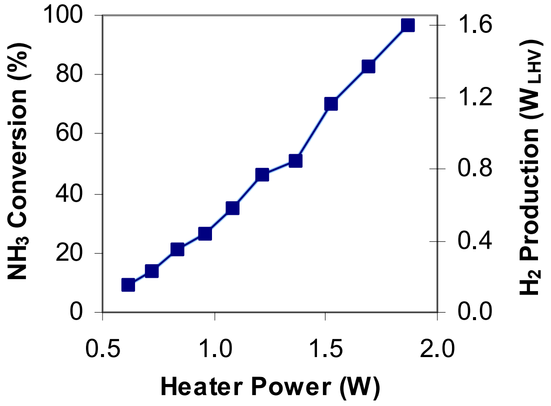

Figure 9. *Ammonia conversion and hydrogen production as a function of applied heater power*

CONCLUSION

MEMS technology offers a very powerful way to make a chemical fuel processor that directly addresses the issue of thermal management. This suspended-tube reactor is highly thermally efficient and has the potential to serve as an efficient catalytic combustor/recuperator for thermoelectric and thermophotovoltaic applications. We have demonstrated the potential of this reactor to be used for hydrogen production by carrying out ammonia cracking with high fuel utilization to produce > 1 W of hydrogen.

ACKNOWLEDGEMENTS

The authors would like to thank the Microsystems Technology Laboratories (MTL) at MIT (in which the majority of the fabrication was performed), the NSF, and the Hertz Foundation. This work was performed under DARPA MEMS contract F30602-99-2-0544.

REFERENCES

[1] P.B. Koeneman, I.J. Busch-Vishniac, and K.L. Wood, *Feasibility of micro power supplies for MEMS. J. MEMS* **6**(4), 1997. p. 355-362.

[2] S.B. Schaevitz, A.J. Franz, K.F. Jensen, and M.A. Schmidt, *A Combustion-Based MEMS Thermoelectric Power Generator*. *Transducers 2001*. Munich, Germany.

[3] A. Mehra, A. Zhang, A.A. Ayon, I.A. Waitz, M.A. Schmidt, and C.M. Spadaccini, *A six-wafer combustion system for a silicon micro gas turbine engine*. *J. MEMS* **9**(4), 2000. p. 517-527.

[4] Geankoplis, C.J., *Transport Processes and Unit Operations*. 1993. Englewood Cliffs, NJ: Prentice Hall, p. 231-232.

[5] Lebouitz, K.S. and A.P. Pisano, *Silicon nitride tubes for fluid flow and bubble growth visualization*, *Proc.-Electrochem. Soc. 98-14 (Microstructures and Microfabricated Systems IV),* 1998. p. 77-86.

[6] Firebaugh, S.L., K.F. Jensen, and M.A. Schmidt, *Investigation of high-temperature degradation of platinum thin films with an in situ resistance measurement apparatus. J. MEMS*. **7**(1), 1998. p. 128-135.