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Short communication

Fabrication of flexible micro-sensors and flow field of stainless steel-based micro-reformer by micro-electro-mechanical-systems process

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ABSTRACT

Recent advances in micro-fuel cells have increased the demand for hydrogen. Therefore, a micro-reformer must be developed. Numerous portable electric devices are extremely small and reformers must therefore be shrunk and combined with micro-fuel cells. The mass production of micro-reformers raises various problems that are yet to be solved, such as the measurement of their internal temperature and flow rate. Such issues influence the efficiency of the micro-reformers. To our knowledge, no investigation has yet properly elucidated the internal operation of micro-reformers. Accordingly, in this work, a flexible micro-temperature sensor, a micro-heater, a micro-flow sensor and the flow field of a stainless steel-based micro-reformer were fabricated by micro-electro-mechanical-systems (MEMS) fabrication technique. The fabrication technique has the advantages of (1) small size, (2) flexible but precise measurement positions, and (3) mass production process.

1. Introduction

Stainless steel has recently been used as a substrate in various fabrication processes for the following reasons. It is easily mass-produced and is inexpensive; it is processed and packaged more easily than a silicon substrate, and it effectively prevents gas leakage. Although stainless steel does not have a better corrosion resistance than silicon or noble metal, it is preferred as a substrate over other metals because of its cost and ease of fabrication.

The reaction between hydrocarbon and water is endothermic, and so the reactant must be heated to induce the reaction. The reaction generates more hydrogen as the temperature is increased. Park designed a steam reformer that exploits external heat [1,2]. This reformer, which is operated at a temperature of 260 °C, has an S/C ratio of 1.1 and a hydrogen production rate of 0.498 mole h^{-1}; it can supply a 15 W fuel cell. Another steam reformer consists of four parts—a fuel evaporation chamber, a heat exchange chamber, a catalyst burning chamber and a steam reforming chamber. The catalyst burning chamber supplies heat to enable the steam reforming chamber to maintain the heat required for reforming. When it is operated at temperatures of 230–260 °C with an S/C ratio of 1.1, its methyl conversion rate is close to 99%, and its hydrogen production rate is 0.88 mole h^{-1}; therefore, it can supply a 59 W fuel cell. Since platinum is required, the production cost is high.

In 2000, Yang [3] utilized bulk-micro-machining to produce micro-channels, and used a platinum thin-film sensor on the micro-channels to measure the distribution of temperature in the channel.

In 2006, Kim and Kwon [4] developed a system that comprised a methanol–steam reformer, a catalytic combustor, a preferential oxidation (PROX) reactor, and a polymer electrolyte membrane fuel cell (PEMFC). A methanol reformer is crucial supplying hydrogen, and it integrates a pre-heater, vaporizing/reforming channels and a catalytic combustor. All components were fabricated using micro-electro-mechanical-systems (MEMS) fabrication technologies combined with catalyst loading processes.

In 2005, Bruschi et al. [5] utilized micro-temperature sensors and micro-heaters on a stainless steel substrate, integrating them with micro-channels and circuit systems. The temperatures upstream and downstream of the channels were measured under various gas flow rates. The results established that when the gas flow rate inside the micro-channels was less than 200 sccm, it was positively correlated with the output voltage of the system.

Scholer et al. [6] employed MEMS to fabricate a micro-platinum flow sensor on glass, and utilized Computational Fluid Dynamics Research Corporation (CFDRC) software to compare and contrast the simulation results with the experimental measurements of flow.

In 2007, Terao et al. [7] applied MEMS to fabricate a micro-flow sensor on a reformer. He utilized water flow to find the measure-

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Table 1
Quantitative conditions of fabrication of a flow field plate of a stainless steel-based micro-reformer.

Step	Recipe
(a)	SS-304, 600 μm-thick
(b)	Evaporate Ti (500 Å) by sputter: power (150 W); pressure (0.2 Pa); deposition temperature (25 °C); deposition rate (1 Å s^{-1})
(c)	Photolithography and define channel: spin photoresist → step 1: 500 rpm, 5 s; step 2: 3000 rpm, 30 s. Soft bake → 90 °C, 300 s. Exposure → 5 mW cm^{-2}. Development → AZ4620:DI water = 1:4. Hard bake → 90 °C, 600 s
(d)	BOE (NH_4F:HF = 6:1) etching Ti; aqua regia (HNO_3:HCl = 1:2) etching SUS: 50 °C; 10 min
(e)	Remove photoresist by acetone
(f)	Remove Ti by BOE

ment range of the sensor, and contrasted the results with the output of a simulation and analysis using 3D-FEM.

In the existing published literature, two different structures have been adopted. The first structure is a cylindrical structure [8,9] in which palladium (Pd) alloy is employed to purify hydrogen directly. The second is a much smaller planar structure [10,11]. The planar reformer design was adopted in this study. Separate studies of stainless steel-based micro-reformers and micro-sensors have been published, but no work has considered them together. Therefore, in this investigation, a flexible micro-temperature sensor, a micro-heater, a micro-flow sensor and the flow field of stainless steel-based micro-reformer were fabricated using the MEMS fabrication technique to minimize their size.

In the authors' other research, micro-flexible temperature and humidity sensors were successfully fabricated on parylene substrate [12]. However, these sensors had the shortcomings of (1) being unable to be utilized in high-temperature (>200 °C) environments; (2) not supporting the use of a wire-bonder to make lines of interconnection between the lines of the pad of the sensor. Accordingly, in this investigation, stainless steel foil (30 μm-thick) was used as a flexible substrate in the process of fabrication to overcome the above shortcomings. It must exhibit high corrosion resistance, high compression resistance, high temperature resistance and high flexibility.

2. Methodology and experiments

The work consists of three main parts. They cover the following topics: (1) fabrication of the flow field plate of a stainless steel-based micro-reformer; (2) fabrication of flexible micro-sensors; (3) calibration of micro-sensors. A 30 μm-thick piece of stainless steel foil is utilized as the substrate of the flexible micro-sensors. MEMS is employed to fabricate the flexible micro-sensors and the flow field plate of the stainless steel-based micro-reformer.

2.1. Fabrication of flow field plate of stainless steel-based micro-reformer

Fig. 1 depicts the fabrication of a flow field plate of a stainless steel-based micro-reformer. Table 1 presents the quantitative conditions of the fabrication of a flow field plate of a stainless steel-based micro-reformer. An E-beam evaporator is employed to evaporate a Ti layer (500 Å) with a thickness of 600 μm onto both sides of a stainless steel 304 substrate. One side of the stainless steel is utilized as the flow field plate; photolithography is adopted to define the pattern, which is then soaked in an etchant (BOE, Buffered Oxide Etch, NH_4F:HF = 6:1) to etch Ti. Aqua regia (HNO_3:HCl = 1:2) is applied in wet etching. The depth and width of the flow channel were 186 μm and 423 μm, respectively, to control the etching time (10 min) and the temperature (50 °C), and enable

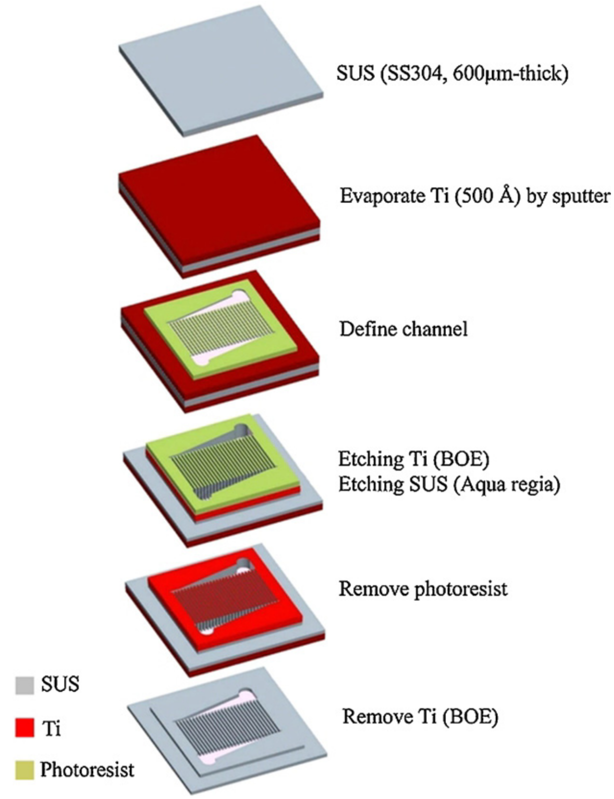

Fig. 1. Fabrication of flow field plate of stainless steel-based micro-reformer.

the liquid to be stirred. Finally, acetone and the etchant of Ti were applied to remove the photoresist and Ti. Fig. 2 displays the flow field plate following etching. The flow field plate has 34 straight micro-channels which are 423 μm wide, 186 μm deep and 34 mm long, as shown in Fig. 2.

The wet etching equipment comprises a water circulation machine, a system for controlling the temperature (50 °C) of the circulating water and a reaction tank. It effectively controls the etching temperature and enables the etchant to be stirred, ensuring the stability of the etching process. Therefore, the roughness, depth and width of the flow channel are more easily controlled. With the etching parameters set herein only 10 min of etching yielded a channel depth of 186 μm. Fig. 3 reveals that the depth and width of the flow channel were 186 μm and 423 μm, respectively, as measured using a surface profiler. Fig. 4 depicts the roughness of the flow channel interior, also measured using a surface profiler: Ra was 3276.6 Å and the maximum Ra was 4092.0 Å. The roughness of the flow channel interior influences the adhesion of the catalyst and the flow field plate of the stainless steel-based micro-reformer. The key factors that affect the roughness are the etching rate and the composition of the etchant.

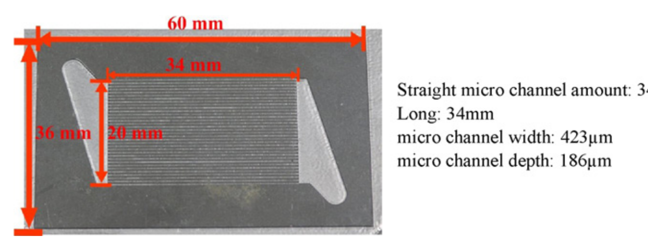

Fig. 2. Flow field plate following etching.

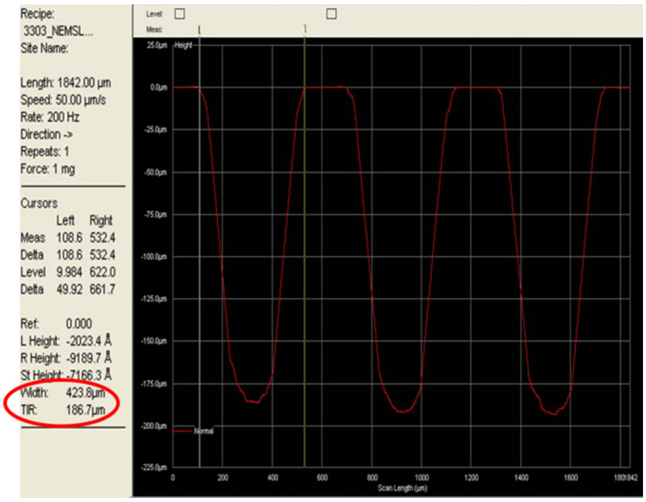

Fig. 3. Depth and width of flow channel, as measured using a surface profiler.

2.2. Function and theory of temperature sensor, heater and flow sensor

Non-contact temperature sensors can be divided into thermal detectors and quantum detectors infrared receiver temperature sensor. A micro-heater mainly consists of a resistive heating wire and conducting electrodes. Platinum and poly-silicon are typically applied as the resistant materials. Gold conducting wires have been utilized between conducting electrodes [13].

The resistance of a general metal is given by

$$R = \rho \frac{L}{A} \tag{1}$$

where R denotes the resistance (Ω); ρ is the resistivity (Ω m); L is the length of the wire (m); A is the cross-sectional area of the wire (m^2). When the resistance varies linearly with the temperature, the relationship between the measured resistance and the temperature change is given by

$$R_t = R_i\,(1 + \alpha\Delta T) \tag{2}$$

where R_t is the resistance at t (°C); R_i is the resistance at i (°C); α is the sensitivity (°C^{-1}) [14,15].

Micro-flow sensors are grouped into thermal flow sensors and non-thermal flow sensors. Thermal flow sensors have three parts—(1) hot wire/hot film anemometer, (2) calorimetric sensor, and (3) time-of-flight flow sensor. All of these parts can be fabricated using MEMS. The micro-thermal flow sensor herein comprised of two micro-temperature sensors and a micro-heater. The purpose of the micro-flow sensor is to measure temperature variations around the micro-heater. The removal of heat flux by the flowing fluid is mostly responsible for the temperature variation, as displayed in Fig. 5.

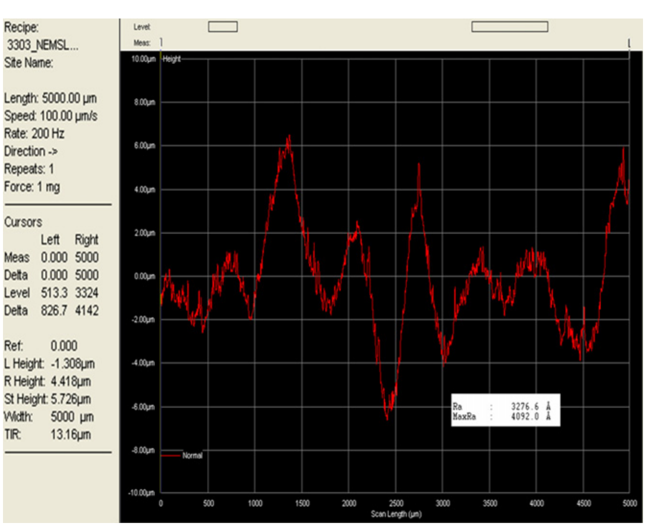

Fig. 4. Roughness of flow channel interior, as measured using a surface profiler.

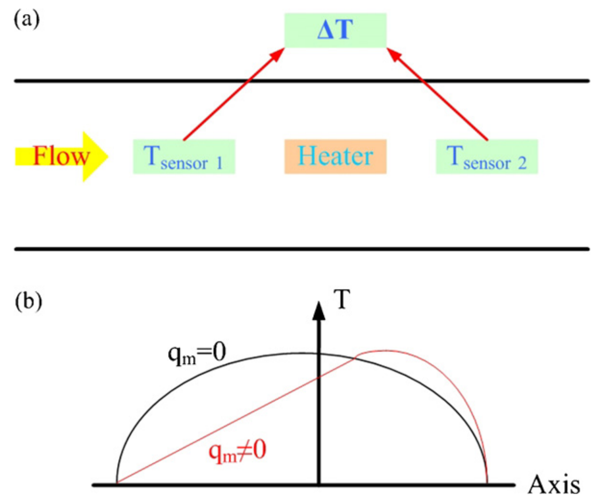

Fig. 5. Principles of operation of thermal micro-fluidic sensor: (a) sketch map of micro-fluidic sensor and (b) temperature distribution of capillary.

The heat flux q_m is expressed as

$$q_m = K \frac{A}{PC_p} \Delta T \tag{3}$$

where P denotes the power consumption of the micro-heater; ΔT is the temperature difference, which can be measured between two temperature sensors that are arranged symmetrically about the micro-heater; C_p is the specific heat at the special pressure; K is the thermal conduction coefficient; A is the revised coefficient of the system. When the fluid flows at a particular velocity, K and C_p can be treated as constants, such that q_m is proportional to ΔT [16,17].

2.3. Fabrication of flexible micro-sensors

Fig. 6 presents the fabrication of a flexible micro-temperature sensor, a micro-heater and a micro-flow sensor. Table 2 presents the quantitative conditions of fabrication of these devices. The substrate of the micro-sensors is made of stainless steel foil (30 µm-thick SS-304). MEMS is utilized to fabricate the micro-sensors on

Table 2
Quantitative conditions of fabrication of a flexible micro-temperature sensor, a micro-heater and a micro-flow sensor.

Step	Recipe
(a)	SS-304 foil, 30 µm-thick
(b)	Evaporate AlN (1500 Å) by sputter: power (200 W); pressure (0.2 Pa); deposition temperature (120 °C); deposition rate (0.5 Å s^{-1})
(c)	Evaporate Cr (200 Å) by E-beam evaporator: pressure (1 × 10^{-5} Pa); emission (6); rotation (30 rpm); deposition rate (0.1 Å s^{-1}). Evaporate Au (2000 Å) by E-beam evaporator: pressure (1 × 10^{-5} Pa); emission (6); rotation (30 rpm); deposition rate (0.3 Å s^{-1})
(d)	Photolithography and define micro-heaters and sensors: spin photoresist → step 1: 500 rpm, 5 s; step 2: 3000 rpm, 30 s. Soft bake → 90 °C, 300 s. Exposure → 5 mW cm^{-2}. Development → AZ4620:DI water = 1:4. Hard bake → 90 °C, 600 s
(e)	KI + I_2 etching Au, Cr-7 etching Cr
(f)	Remove photoresist by acetone

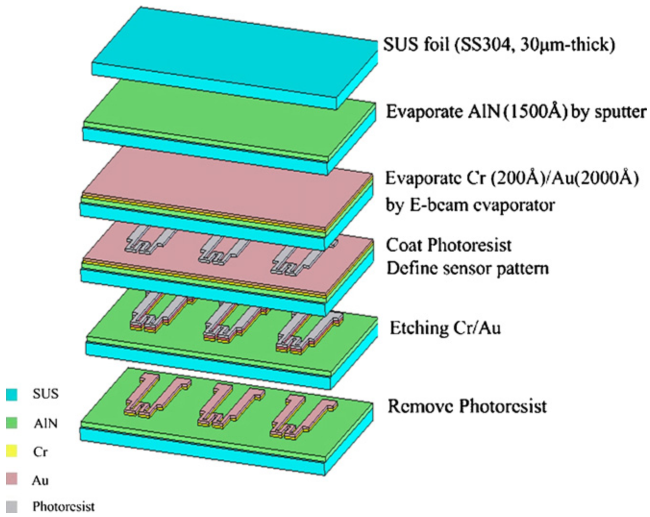

Fig. 6. Fabrication of flexible micro-sensors.

the flexible substrate. In the fabrication, sulfuric acid and hydrogen peroxide are first utilized to clean the stainless steel foil; the photoresist is spun and lithography performed to define the pattern of the micro-sensors. Then, aluminum nitride (AlN) is sputtered as a bottom insulation layer with a thickness of 1500 Å. Aluminum nitride was employed as an insulation layer because of its excellent insulating properties and high thermal conductivity. Then, the lift-off procedure was adopted to remove the photoresist. An E-beam evaporator was then used to evaporate chromium (Cr) as an adhesion layer between AlN and gold (Au), with a thickness of 200 Å, and evaporated gold (Au) formed micro-flow sensors with a thickness of 2000 Å upon wet etching. Finally, the photoresist was spun to produce an insulating layer, and the micro-flow sensors were connected by an Al wire to make measurements.

3. Results and discussion

In this work, the MEMS technique was applied to fabricate the flow field plate of a stainless steel-based micro-reformer and flexible micro-sensors on a stainless steel foil (30 μm-thick). Figs. 7 and 8 display photographs of micro-sensors. Wet etching is utilized to generate a flow field plate of stainless steel. The flow channel is etched using aqua regia. The etching rate increases with the temperature of the aqua regia. The amounts of HNO_3 and HCl also influence the etching rate and the roughness of the interior of the flow channel. The etching equipment effectively controls the etching temperature and enables the etchant to be stirred, increasing the stability of the etching process. Therefore, the roughness, depth and width of the flow channel are more easily controlled. Given the etching parameters in this work, only 10 min of etching yielded a channel depth of 186 μm.

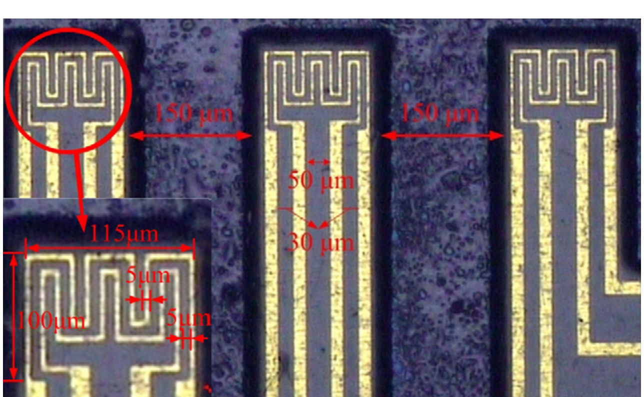

Fig. 7. Optical microscopic photograph of flexible micro-sensors.

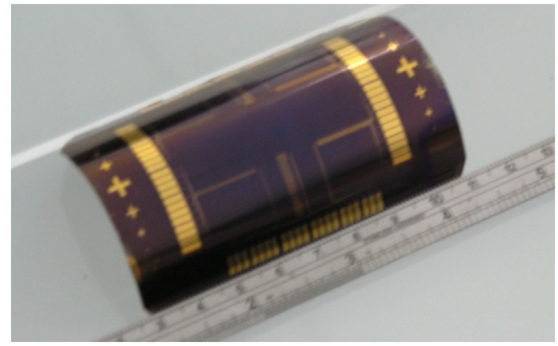

Fig. 8. Final flexible micro-sensor products.

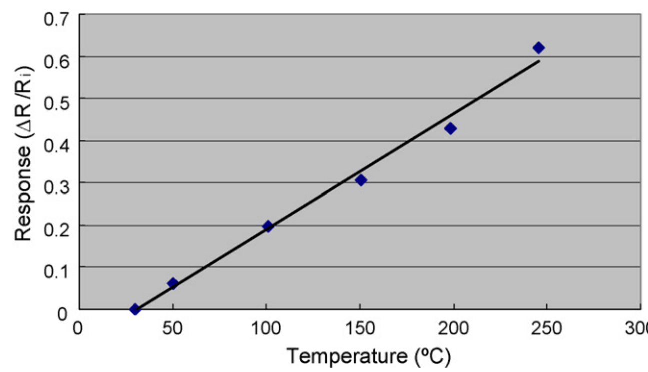

Fig. 9. Correction curve of micro-temperature sensor.

For calibration, the flexible micro-sensors were initially connected to a 4230 LCR meter. The micro-sensors were then placed in a programmable temperature chamber (with an accuracy of 0.5 °C). The temperature in the chamber was controlled to measure the variation of the output resistance of the LCR meter under the operating conditions. Experimental results demonstrate that the resistance was linearly related to the temperature, as shown in Fig. 9.

4. Conclusion

In this study, a flexible micro-temperature sensor, a micro-heater and a micro-flow sensor were fabricated using MEMS fabrication technique. The fabrication technique has the advantages of (1) small size, (2) flexibility but precision of measurement positions, and (3) mass production process. Furthermore, only gold was used herein to produce the micro-sensors, simplifying the fabrication process and reducing its cost. The aqua regia etching was also investigated to evaluate its capacity to control the depth, width and roughness of a stainless steel flow-channel. The depth of the channel could be controlled accurately. The maximum variation of the depth of the channel was less than 1%. Future study will evaluate the operating parameters of flexible micro-temperature sensors, heaters and flows sensors in a micro-reformer to improve the design and performance of micro-reformers.

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